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THE

# PHYSICAL REVIEW.

## ON THE PHOTOMETRY OF DIFFERENTLY COLORED LIGHTS AND THE "FLICKER" PHOTOMETER.[1]

By Frank P. Whitman.

In November, 1893, during measurements on some colored disks, it became necessary to know the relative luminosities of the colored papers employed. An attempt was first made to estimate the luminosity directly by comparison with Maxwell disks of black and white, smaller in diameter, and mounted on the same axis. The relative proportions of black and white were changed until, on rotation, they formed a gray, which was estimated to be about equal in brightness to the colored disk under examination. This method, practiced by certain experienced observers, doubtless has afforded good results, but in my hands proved difficult and uncertain.

Trials were then made by four other observers, all somewhat skilled in physical measurement, whose general color-sense was found to be similar, but their estimates of luminosity were found to vary in such an irregular fashion as to make any comparison impossible.

Later experiments, carried out with the help of some thirty undergraduate students, led to similar results. Differences of 50 per cent between two different observers frequently arose,

[1] Read at the Springfield meeting of the A. A. A. S., Aug. 30, 1895.

when the light to be compared differed no more than an ordinary from a Welsbach gas-burner; while the same observers, working with light of the same color, would agree at least within 2 or 3 per cent.

By practice the margins of difference may be rendered smaller, yet experts often differ in their estimates of the brightness of arc lights when compared with standards of different color; and it is questionable whether one can always be sure that by practice in such measurements he gains greatly in accuracy. His measurements agree with each other better than at first, but if his method of comparison have in it something of an arbitrary or personal quality, as it must from the very nature of the case, it remains uncertain whether he may not be fixing himself in an erroneous practice rather than approaching a correct one.

The character of these results, and the need of some more exact method of comparing color-luminosities, led to the consideration of Professor Rood's "flicker" experiments.[1]

Rood prepared about fifty gray disks differing successively, as equally as possible, in depth of tint from black to white. If a dark shade was combined with a light shade in the usual way, and rotated rather slowly, the familiar unpleasant sensation known as a flicker was produced; but if successive pairs, more and more nearly alike, were chosen, the flicker became less, until it almost or quite disappeared. Nearly the same effect was produced if, instead of a gray, some other color was substituted on one of the disks. It was always possible to combine with it a gray disk of such a shade that the flicker nearly ceased, showing that this sensation is apparently independent of the wave-lengths of the lights compared, and dependent only on their relative luminosities. Professor Rood suggests that the principle may be easily applied to ordinary photometric work, but indicates no method. The special arrangement described in his paper serves admirably to compare pigments, when in such form that they can be spread upon disks and mounted in the whirling machine.

For ordinary photometric purposes, however, there is necessary some arrangement by which luminosity can be varied continuously

[1] American Journal of Science, Vol. XLVI., September, 1893.

instead of step by step, as with a set of gray disks, which can be mounted on a photometer bar so as to compare colored lights as well as colored pigments, and which is reasonably quick and convenient in use. No doubt there are many ways of applying Professor Rood's flicker principle; the one which I, after some trial, found most successful was as follows: —

A card was cut in the shape *AHBG*, in the figure, so as to form two semicircles of about 5 and 8 cm. radius respectively, joined along a common diameter. This could be rotated at any desired speed about the axis *K*, in earlier experiments by clock-

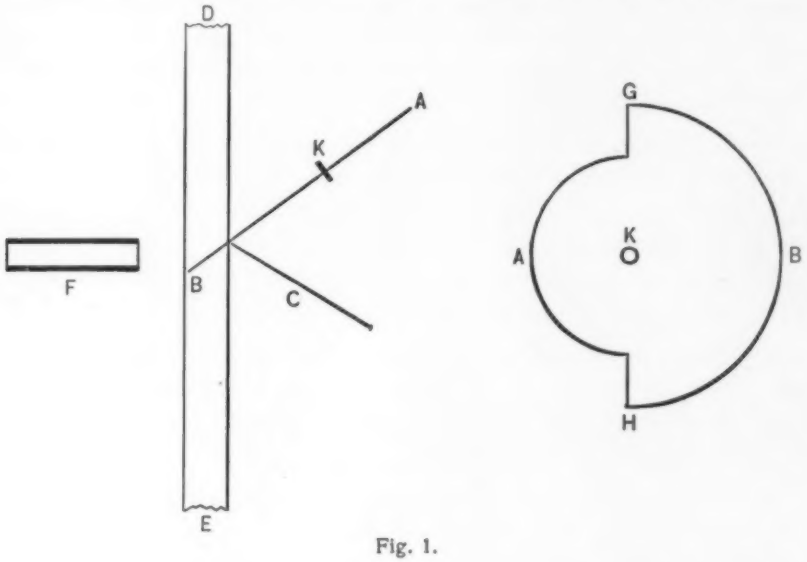


Fig. 1.

work, but afterward, and more conveniently, by hand. A diagrammatic plan of the apparatus as used is shown in the figure. *DE* represents the photometer bar, *AB* is the revolving disk, *C* is a card, which may be white or colored with any pigment which it is desired to study, *F* is a tube through which the observer looks. It is evident that when the apparatus is in the position shown in the figure, the outer portion of the revolving disk only will be visible through the tube, but when the disk is rotated half a turn, the small semicircle will not come into view at all, and the observer will see only the card *C*. As the disk revolves, the two pieces will

be presented to the eye in rapid succession, and, if they differ in luminosity, will produce the sensation of "flicker." If equal lights are placed at the ends of the photometer bar, the relative illumination of the card and disk can be varied by sliding the photometer along the bar. The flickering sensation can thus be entirely destroyed, whatever the colors are upon the card and disk. (Various colors were tried upon the disk, — red, white, and different grays, — but white was finally adopted as in all cases the most convenient.) When the proper position of the photometer was reached, not only did the flicker vanish, but the sense of color in the field of vision became much weaker or entirely disappeared, so

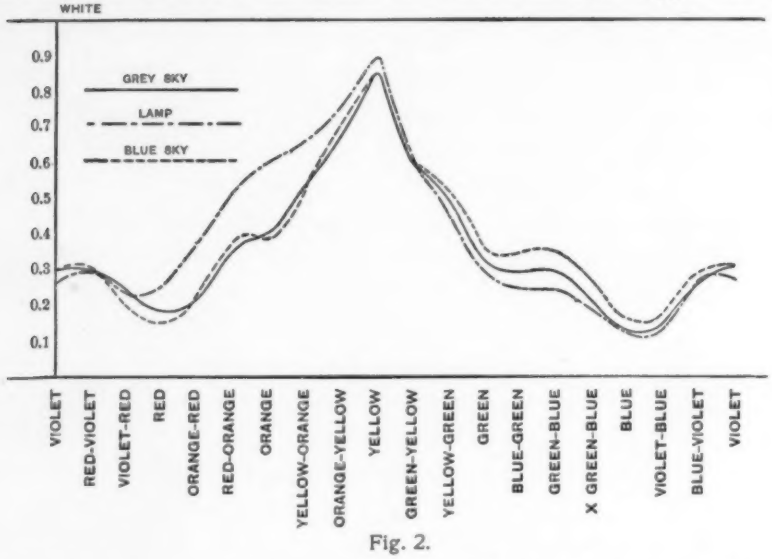


Fig. 2.

that it was frequently difficult or impossible to tell what color was upon the card. A slight movement of the photometer in either direction revived the sense of color and reëstablished the flicker. The results obtained with this instrument were surprisingly good in ease, rapidity, and precision.

Work was interrupted at this point until May, 1895, when the measurements were taken up again, and the instrument itself somewhat carefully studied.

The colors used for experiments on pigments were chosen from the well-known series of colored papers made by the Milton Brad-

ley Company of Springfield, Mass., and included the whole range of the spectrum. These papers were pasted upon perfectly flat cards, and placed successively in the position marked *C* in the figure. Three curves are shown to illustrate the capacity of the instrument, exhibiting the relative luminosities of these nineteen colors, when illuminated by the light of a kerosene lamp, of a dull gray sky, and of a bright blue sky.

The predominance of the lamp-curve toward the red end of the spectrum and of the clear sky at the other end is manifest, while the similarity of the curves shows that the measurements are of like character and definiteness, whatever the source of illumination. In all these cases the revolving disk was white, lighted by a lamp, while the colors on the card were exposed to the light under investigation. Since the flicker effect is independent of the wave-length, any source of light which is constant may be used to illuminate the disk without changing the results dependent on the luminosity of the colored card. The curves from sky light and cloud light, though the mean of several trials, were not entirely satisfactory on account of the comparatively inconstant brightness of these sources of light. The observations on lamplight, however, were made twice, at an interval of over two months, with practically identical results.

A greater interest, perhaps, lies in the instrument itself. An apparatus so new, and depending on a physiological principle which has been so little studied, presents many points for investigation, before its utility as a practical photometric apparatus is assured. The remainder of this paper is occupied with a study of some of these points.

1. The precision of setting, as compared with other types of photometer, was tested in over one hundred settings on nineteen different colors. The difference between two successive readings was seldom more than one per cent, though a few readings differed as much as two or three per cent. As these readings were made over the whole range of the spectrum, it seems fair to say that the instrument can be used upon lights presenting the widest differences of wave-length, with a precision approaching that of ordinary types of photometer when comparing lights of the same color.

2. Since the photometer depends, not on the actual comparison of like quantities, but on the distinctness of a peculiar physiological sensation, — the flicker, — it is worth while to see whether different observers will agree. To test this question, and incidentally to try the instrument with colored lights instead of colored papers, both disk and card were made white, and equal lamps, the colors of which could be changed at pleasure by the interposition of colored glass, were placed at the ends of the photometer bar. Two observers, whose eyes were known to be similar, compared successively the brightness of the two naked lamps, first by an ordinary photometric method, then by the flicker. A red glass was then placed in front of one lamp, a green glass in front of the other, and the same observations were made again. One of the two observers had never seen the instrument before. The results follow, each being the mean of four or five concordant observations. The actual readings are given in feet and hundredths, not reduced to comparative luminosities. One lamp stood at 3.00, the other at 9.00 on the photometer bar.

| OBSERVER F. | | OBSERVER W. | |
|---|---|---|---|
| Ordinary. | Flicker. | Ordinary. | Flicker. |
| Both lights naked. | | | |
| 5.98 | 5.96 | 5.98 | 5.98 |
| Left lamp red, right green. | | | |
| 5.59 | 6.79 | 6.08 | 6.88 |

Thus, in the last case, the setting of F by direct estimation differed from that by flicker by 1.20 feet, that of W by 0.80 foot.

The setting of F by estimation differed from that of W by 0.49 foot ; while F's flicker setting differed from W's by only 0.09 foot. The last disagreement is comparable with the errors of observation.

At a later time, three other observers, making comparisons for technical purposes between coal-oil lamps and a standard candle which differed from them somewhat in color, were able with the flicker photometer to obtain accordant results among themselves much more easily and surely than by ordinary methods.

3. Two "disks" like those in the cut were mounted on the same axis in the photometer. By sliding one upon the other, the fraction of a revolution during which the card was visible could be varied between 180° and 0°. The relative length of exposure of the eye to the two lights could thus be varied within wide limits. Several comparisons were made of lights differing widely in color, and with openings from 22½° to 180°, but no differences in reading were observed that could be traced to this cause. While it is true that the sensitiveness of the retina differs for lights of different wave-lengths, and probable that differently colored lights require different periods of time to produce equal sensations in the eye, it appears from these experiments that there is time, at the comparatively slow rate of rotation of the disk, for every color to produce its full effect, so that errors which might be produced by irregularity in rate of rotation or in shape of the disk are negligible.

4. In much of the work, the photometer and the standard lamp were kept at fixed points, and the balance obtained by moving the other light, thus making all comparisons at the same actual degree of illumination. This method of using any photometer has some obvious advantages, though the sensitiveness is not quite so great as when the photometer itself is moved. To determine whether the absolute brightness has any effect on the settings, measurements were made of six colors — red, orange, yellow, green, blue, violet — under widely differing illuminations. When the light was faint the measurement became much more difficult, but the results obtained with bright and faint light did not appreciably differ, showing that the well-known greater sensitiveness of the eye to blue light is not important in measurements made under conditions proper to this photometer. When the illumination is small the flicker is very faint and may be invisible while the photometer is moved over as much as 6 or 8 cm., but by reading the points each side of this space where the flicker again becomes visible, and taking the mean of the two readings, results may be obtained almost as trustworthy as with brighter light. It should be remarked that this method in general depends for its value somewhat on the state of the eye. It appears certain that

two normal eyes, in a reasonably fresh condition, would obtain like results, but if the eye is wearied from long-continued observation or loss of sleep, the perception of the flicker becomes more difficult, and the difficulty appears to vary with different colors in a way that has not yet been studied.

5. The question still remains, whether the flicker method gives in all cases a true measure of luminosity comparable to that which would be obtained by any more direct photometric method. To test this, the luminosity measures afforded by Maxwell's disks were used.

Suppose, for example, three colors — say red, green, blue — combined on the whirling machine into a neutral gray, which is matched by the combination of a black and a white disk. The amount of white in the latter combination, corrected for the white light reflected by the black portion, is of course the measure of the luminosity of the colored disk in terms of white, which quantity, again, is dependent upon the luminosities of the three colors of which it is composed.

If now the fraction of the whole circle occupied by any color is multiplied by its luminosity as measured with the flicker photometer, the result will be the amount of white equivalent to that colored sector, and the sum of the results obtained by treating each of the colored sectors in this way should equal the amount of white in the black and white disk. Two examples are given below. The circumference of the disk was divided into one hundred equal parts, so that the numbers given are direct percentages of the whole circle.

The upper row of figures in each case is the ordinary color-disk equation. The second is the luminosity of the given colors referred to white, as measured by the flicker, the lower line gives the product in each case. The sum of these products given under white should be the same as the white in the upper row, which is the corrected reading from the black and white Maxwell disks.

| | Red. | Green. | Blue. | White. | Red. | Green-Yellow. | Blue. | White. |
|---|---|---|---|---|---|---|---|---|
| Color-equation | 40.5 | 49.2 | 10.3 | 22.6 | 18.5 | 34.0 | 47.5 | 30.4 |
| Luminosity | 0.238 | 0.295 | 0.106 | — | 0.238 | 0.617 | 0.106 | — |
| | 9.64 | 14.50 | 1.09 | 25.23 | 4.41 | 20.96 | 5.03 | 30.40. |

Fourteen such trials were made with different colors, the results differing by one to three per cent from exact equality.

*Summary.*

The flicker photometer used to compare lights of any color approximates in convenience and accuracy any of the ordinary photometric appliances used with lights of the same color. Different observers whose vision is normal obtain like results.

Irregularities in the division of the disk or the rate of rotation are without appreciable effect on the precision of the measurements.

Differences in the absolute brightness of the lights compared present no greater difficulties than in any photometric method.

The instrument gives a true measure of luminosity comparable with that obtained in other trustworthy ways.

ADELBERT COLLEGE, Nov. 1, 1895.

# THE CHEMICAL POTENTIAL OF THE METALS.

BY WILDER D. BANCROFT.

IN a previous paper[1] I have communicated the numerical values of the electromotive force of certain cells, consisting of two metals and a single solution. It is now desirable to consider the relation between these single-liquid polarizable cells and the corresponding constant reversible cells of the Daniell type. According to the theory of Nernst, the potential difference between a metal and a solution of a salt of that metal is given by the expression[2]

$$\pi = \frac{RT}{ne} \log \frac{P}{p} \times 10^{-4} \text{ volts},$$

where $\pi$ is the potential difference, $n$ the valency of the kation, $p$ its partial osmotic pressure, $e$ the quantity of electricity transported by a gram-equivalent, and $P$ the solution pressure of the electrode metal. The electromotive force of a cell of the Daniell type $M_1|p_1M_1X|p_2M_2X|M_2$ will be the algebraic sum of the two potential differences between the metals and the solutions, plus the difference of potential between the solutions. I leave out of account a possible potential difference between the metals, as this term is negligible so far as our present knowledge goes. The electromotive force of this type of cell will be

$$\pi = \frac{RT}{ne}\left(\log \frac{PM_1}{PM_2} + \log \frac{p_2}{p_1}\right) \times 10^{-4} + z \text{ volts},$$

where $z$ represents the difference of potential between the solutions, and the valency of the metals $M_1$ and $M_2$ is the same. If the wandering velocities of the ions $M_1$ and $M_2$ are nearly equal,

[1] Zeitschr. f. ph. Chem., 12, 289, 1893. Through a misprint on p. 290, the correction for Pb|Hg in NaI, and Bi|Hg in NaCl, reads 0.25 and 0.75 volts, instead of 0.025 and 0.075 volts respectively.

[2] Ibid., 4, 148, 1889.

and $p_1$ and $p_2$ be made so, the value of $\varepsilon$ approaches zero, while the term $\log \frac{p_2}{p_1}$ drops out entirely. The electromotive force of the cell, $M_1|pM_1X|pM_2X|M_2$, is given very nearly by the expression

$$\pi = \frac{RT}{ne} \log \frac{PM_1}{PM_2} \times 10^{-4} \text{ volts},$$

and is independent of the absolute concentration of the salts $M_1X$ and $M_2X$. Let us take as a concrete case the cell $Zn|ZnSO_4|CuSO_4|Cu$, and let the concentrations of the zinc and copper sulfates always be equal. It has been found experimentally that the electromotive force of this cell is independent of the absolute concentration.[1] Suppose that instead of diluting the two solutions with pure water, we add a solution of $K_2SO_4$. According to Nernst's theory, this will have no influence on the electromotive force, except in so far as it affects the dissociation of the two sulfates, and thereby the concentrations of the Zn and Cu ions. If the dilution be carried far enough, we shall come at last, without change of electromotive force, to the cell with neither zinc nor copper sulfate, to the cell $Zn|o\ ZnSO_4 + x\,K_2SO_4|o\ CuSO_4 + x\,K_2SO_4|Cu$, which is the same as the cell $Zn|x\,K_2SO_4|Cu$. In other words, the one-liquid, non-reversible cells are the limiting cases of the two-liquid, reversible cells in which the concentrations and wandering velocities of the reversible ions are equal, the dissociation being assumed to be complete. This last clause is necessary; for if the percentage dissociations of the zinc sulfate and copper sulfate were different, equal concentrations of the two sulfates would not correspond to equal concentrations of zinc and copper ions, and this would affect the potential difference between the solutions. The concentration of the $K_2SO_4$ should have no effect, and it was shown in my previous paper[2] that this was the case. It is clear that in measurements made with two-liquid, reversible cells, there are two sources of error besides those due to the surface conditions of the electrodes. These are differences of concentration and differences of wandering velocities.

[1] Wright, Phil. Mag. (5), 13, 265, 1882.

[2] Zeitschr. f. ph. Chem., 12, 294, 1893, Tables II., V.

The effects of these two errors are that the terms $\log \frac{p_2}{p_1}$ and $z$ do not disappear. The determinations made with single-liquid cells are free from these sources of error; but the difficulties due to polarization are so great that the variations are apt to be much larger than in measurements made with two-liquid, reversible cells. In Table I. are some of the results obtained with the two styles of cells. In the first four columns are the measurements of Paschen,[1] myself, Overbeck and Edler,[2] Ostwald,[3] all made with single-liquid cells. In the next three are the figures of Wright and Thompson,[4] Neumann,[5] Braun,[6] with reversible cells. In the eighth are the data of Magnanini,[7] and in the ninth those of Regnauld,[8] the former being for polarizable, the latter for non-polarizable cells.

TABLE I.[9]

| Electrodes. | Electrolyte. | Paschen. | W. D. B. | O. & E. | Ostwald. | W. & T. | Neumann. | Braun. | Magnanini. | $D = 100$. Regnauld. |
|---|---|---|---|---|---|---|---|---|---|---|
| ZnCd | Chlorides | 0.296 | 0.333 | 0.368 | 0.360 | 0.330 | 0.329 | 0.334 | 0.32 | 0.235 |
| ZnCd | Bromides | 0.293 | 0.333 | 0.364 | 0.340 | 0.315 | — | 0.256 | 0.30 | 0.235 |
| ZnCd | Iodides | 0.298 | 0.331 | 0.365 | 0.304 | 0.322 | — | 0.262 | 0.20 | 0.235 |
| ZnCd | Sulfates | 0.35 | 0.334 | 0.430 | 0.401 | 0.360 | 0.362 | 0.33–37 | 0.36 | 0.307 |
| ZnCd | Nitrates | — | 0.332 | 0.446 | 0.411 | 0.352 | 0.352 | 0.27–37 | 0.38 | 0.235 |
| ZnCd | Acetates | — | 0.332 | — | 0.373 | — | — | 0.336 | — | — |
| ZnPb | Chlorides | 0.512 | 0.526 | 0.561 | 0.610 | *0.591 | *0.598 | — | 0.51 | — |
| ZnPb | Bromides | 0.525 | 0.528 | 0.541 | 0.599 | 0.571 | — | — | 0.45 | — |
| ZnPb | Iodides | 0.545 | [1]0.527 | 0.558 | 0.587 | 0.455 | — | — | 0.38 | — |
| ZnPb | Sulfates | 0.525 | 0.527 | 0.502 | 0.592 | *0.50–55 | — | — | 0.51 | — |
| ZnPb | Nitrates | — | 0.526 | 0.589 | 0.598 | 0.585 | 0.589 | 0.44 | 0.51 | — |
| ZnPb | Acetates | — | [1]0.527 | — | 0.638 | 0.607 | 0.601 | 0.54–58 | — | — |
| CdPb | Chlorides | 0.216 | 0.195 | 0.192 | 0.249 | *0.260 | *0.269 | — | — | — |
| CdPb | Bromides | 0.232 | 0.194 | 0.181 | 0.259 | 0.256 | — | — | — | — |
| CdPb | Iodides | 0.247 | [1]0.194 | 0.188 | 0.256 | 0.24 | — | — | — | — |
| CdPb | Sulfates | 0.18 | 0.194 | 0.17 | 0.191 | *0.13–17 | — | 0.18–22 | — | — |
| CdPb | Nitrates | — | 0.193 | 0.243 | 0.187 | 0.233 | 0.237 | 0.240 | — | — |
| CdPb | Acetates | — | [1]0.194 | — | 0.265 | — | — | — | — | — |

[1] Wied. Ann., 43, 590, 1891.
[2] Ibid., 42, 209, 1891.
[3] Zeitschr. f. ph. Chem., 1, 583, 1887.
[4] Phil. Mag. (5), 19, 1, 1885.
[5] Zeitschr. f. ph. Chem., 14, 193, 1894.
[6] Wied. Ann., 16, 575, 1882.
[7] Rend. Acc. Linc., 6, 182, 1890.
[8] Wiedemann Electrizität (2. Aufl.), 1, 792.
[9] Values marked [1] are calculated from the other experiments and are not direct observations.

The agreement is not so striking as one might wish; but it is sufficient. The values marked with a star are not properly comparable, because the two solutions were not of the same concentration. Nernst's formula for the cells we have been discussing is

$$\pi = \frac{R\tau}{n\epsilon} \log \frac{Pm_1}{Pm_2} \times 10^{-4} \text{ volts.}$$

It is, therefore, necessary to consider the nature of $\log P$. Nernst has not made any direct statement, so far as I know, about a possible connection between $\log P$ and the negative ion of the salt solution. Ostwald[1] and his pupils look upon $\log P$ as a function of the electrode metal and the temperature only, and hold that it is independent of the nature of the negative ion. If this be so, we ought to find that all cells of the type $M_1|pM_1X|pM_2X|M_2$, should have the same value so long as $M_1$ and $M_2$ remained the same and that a change in $X$ should have no effect, barring secondary disturbances such as differences of wandering velocities, of dissociation, etc. In the non-reversible cells $M_1|RX|M_2$, where these disturbing influences are eliminated, this should be even more noticeably true. That this is the case for certain metals, I have already shown.[2] The results of other investigators, as given in Table I., show this same thing, though not quite so clearly. The values for Zn|Cd in solutions of chlorides, bromides, and iodides are found to be identical by Paschen, by Overbeck and Edler, and by Regnauld, though the three sets differ hopelessly in absolute value. Braun makes the bromides and iodides the same, and puts the chlorides, sulfates, and nitrates in a group together.

There is not the same agreement among the reversible cells in which Pb forms one of the electrodes; but this is due in part to the insolubility of the lead salts. With the polarizable cells things are much clearer, though the discrepancies between the values found by different observers complicates matters very much. Ostwald finds practically the same value for Zn|Pb in all solutions except acetates. Paschen makes the bromides and sulfates the same, while Overbeck and Edler find the chlorides and iodides

[1] Lehrbuch, II., 855.

[2] Zeitschr. f. ph. Chem., 12, 294, 1893, Table III.

identical. On the whole we may say that the theory of Nernst has predicted the facts with great accuracy thus far. If, however, the single-liquid cells are the limiting cases of the two-solution reversible cells, and if $\log P$ is a function of the electrodes and temperature only, the electromotive force should always be independent of the nature of the negative ion of the salt solution. That this is not so will be seen from Table II.

TABLE II.

| Electrodes. | Electrolytes. | Paschen. | W. D. B. | O. & E. | Ostwald. | W. & T. |
|---|---|---|---|---|---|---|
| ZnHg | Chlorides | 1.112 | 1.151 | 1.121 | 1.173 | 1.12–26 |
| ZnHg | Bromides | 0.983 | 0.991 | 0.996 | 1.036 | 0.972 |
| ZnHg | Iodides | 0.846 | 0.847 | 0.830 | 0.841 | 0.801 |
| ZnHg | Sulfates | 1.300 | 1.302 | 1.302 | 1.484 | 1.46–51 |
| ZnHg | Nitrates | — | 1.200 | 1.330 | 1.422 | 1.499 |
| ZnHg | Acetates | — | 1.228 | — | 1.451 | — |
| CdHg | Chlorides | 0.816 | 0.818 | 0.755 | 0.813 | 0.812 |
| CdHg | Bromides | 0.690 | 0.659 | 0.632 | 0.696 | — |
| CdHg | Iodides | 0.548 | 0.515 | 0.465 | 0.535 | — |
| CdHg | Sulfates | 0.968 | 0.969 | 0.962 | 1.083 | — |
| CdHg | Nitrates | — | 0.867 | 0.884 | 1.011 | — |
| CdHg | Acetates | — | 0.898 | — | 1.078 | — |

The variation in passing from a chloride to an iodide solution is about 0.3 volts, far more than can be accounted for by any experimental error. This necessitates a reconsideration of the Nernst hypothesis to see where the flaw in the reasoning occurs. The assumption made is that, if a metal be dipped into a solution of one of its salts, the metal will go into solution, and the electrode become charged negatively towards the electrolyte, if the "solution pressure" of the metal is greater than the osmotic pressure of the corresponding ion in the solution. If the latter is greater than the "solution pressure," ions will be precipitated upon the metal which would become positive to the solution. This reasoning is applicable to zinc in a solution of potassium chloride, for instance. The initial concentration of the zinc ions in the solution is zero, and the metal will therefore send off ions until the potential difference

corresponding to equilibrium is reached. This will not be the case when we consider mercury in a solution of potassium chloride. There are no mercury ions in solution to precipitate on the metal, and it remains an unanswered problem how the mercury is to become charged positively in respect to the solution. Yet this takes place and the value of the potential difference, as determined by the dropping-mercury electrode method, is a perfectly well defined one. This value should be independent of the nature of the salt solution if Ostwald's assumption about log $P$ is correct. This is not the case. In this connection I may say that the question as to the value of the dropping-mercury electrode as a means of measuring single potential differences does not affect this discussion at all. It is an experimental fact that the sum of the potential differences $M_1|RX$ and $RX|M_2$, as determined by this method is equal to the electromotive force of the cell $M_1|RX|M_2$ and it is immaterial for the present purposes whether the single determinations are wrong by a constant amount, as I am only considering variations in the values. I will now try to show what conclusions may be drawn from the measurements of Paschen[1] on the potential differences between metals and salt solutions not containing the metal of the electrode as ion. He points out himself that the potential difference is not a function of the positive ion of the salt solution. It is not a function of the concentration. Paschen inclines to the opposite view; but I think he is wrong and that his own results as tabulated in Table III. will bear me out. The first column gives the nature and concentration of the solution; the second, third, and fourth the potential differences between the metals, mercury, zinc, and cadmium, and the solution. Mercury is positive towards the solution, zinc and cadmium negative.

[1] Wied. Ann., 43, 590, 1891.

TABLE III.

| Solution. | Sol\|Hg | Zn\|Sol | Cd\|Sol | Solution. | Sol\|Hg | Zn\|Sol | Cd Sol |
|---|---|---|---|---|---|---|---|
| HCl = 1 l. | 0.560 | 0.560 | 0.248 | $H_2SO_4$ = 200 l. | 0.825 | 0.668 | 0.261 |
| = 10 | 0.551 | 0.610 | 0.272 | HBr = 0.272 | 0.503 | 0.393 | 0.175 |
| = 100 | 0.584 | 0.643 | 0.242 | = 0.983 | 0.490 | 0.423 | 0.202 |
| KCl = 0.28 | 0.524 | 0.525 | 0.260 | = 10 | 0.493 | 0.567 | 0.238 |
| = 1 | 0.539 | 0.547 | 0.249 | = 100 | 0.496 | 0.610 | 0.246 |
| = 10 | 0.553 | 0.575 | 0.251 | KBr = 0.402 | 0.474 | 0.399 | 0.203 |
| = 100 | 0.584 | 0.523 | 0.240 | = 1 | 0.483 | 0.441 | 0.186 |
| NaCl = 0.239 | 0.562 | 0.521 | 0.262 | = 10 | 0.493 | 0.422 | 0.167 |
| = 1 | 0.556 | 0.512 | 0.266 | = 100 | 0.505 | 0.496 | 0.183 |
| = 10 | 0.557 | 0.541 | 0.268 | HI = 10 | 0.411 | 0.427 | 0.117 |
| = 100 | 0.590 | 0.557 | 0.268 | = 100 | 0.417 | 0.515 | 0.159 |
| $MgCl_2$ = 0.971 | 0.546 | 0.525 | 0.252 | = 1000 | 0.386 | 0.584 | 0.214 |
| = 2 | 0.547 | 0.531 | 0.277 | KI = 0.795 | 0.400 | 0.250 | 0.113 |
| = 20 | 0.548 | 0.598 | 0.258 | = 1 | 0.400 | 0.233 | 0.113 |
| = 200 | 0.580 | 0.516 | 0.245 | = 10 | 0.412 | 0.308 | 0.110 |
| $BaCl_2$ = 0.809 | 0.562 | 0.512 | 0.259 | = 100 | 0.412 | 0.369 | 0.120 |
| = 2 | 0.555 | 0.554 | 0.249 | = 1000 | 0.386 | 0.454 | 0.199 |
| = 20 | 0.553 | 0.583 | 0.281 | $K_2SO_4$ = 2.152 | 0.700 | 0.618 | 0.287 |
| = 200 | 0.586 | 0.566 | 0.240 | = 20 | 0.720 | 0.573 | 0.274 |
| $H_2SO_4$ = 2 | 0.835 | 0.653 | 0.319 | = 200 | 0.730 | 0.592 | 0.252 |
| = 20 | 0.817 | 0.668 | 0.284 | | | | |

The values for Sol|Hg are identical for dilutions of 1 l. and 10 l. with the exception of KCl, KBr, $K_2SO_4$, and $H_2SO_4$; the variations for $K_2SO_4$ and $H_2SO_4$ are in opposite directions and certainly due to experimental error. There is no reason to assume that KCl is different in behavior, theoretically, from NaCl or $BaCl_2$, and we must conclude that this discrepancy is also accidental. In passing from dilutions of 10 l. to those of 100 l. there is a distinct increase in potential difference between mercury and chloride solutions. With the other solutions the change is either non-existent or much less marked. On the other hand, cadmium shows this behavior only with HI and KI solutions, zinc with HCl, NaCl, HBr, KBr, HI, and KI solutions. The solutions of HBr, KBr, HI, and KI are not the ones where mercury shows a marked change of value with increasing dilution, so that there is no qualitative regularity in the phenomena. As there is also no

quantitative connection to be detected between the change of concentration and the change of potential difference, and as the experimental error is very large in the case of determinations with dilute solutions, I see no reason to assume that there is any change of potential difference, at any rate within wide ranges of concentration.[1] I am led to this conclusion the more strongly because, if we admit with Paschen that the potential difference increases with increasing dilution, we must admit that the electromotive force of the cell Cd|KCl|Hg is a function of the concentration, and I have already shown that this is not the case.[2]

Paschen has pointed out that these potential differences are functions of the metal forming the electrode and of the anion. This can hardly be accounted for on the Ostwald-Nernst hypothesis. If the potential difference between Hg and KCl or KBr solutions are due to the amount of mercury as ion which has gone into solution, we must say that the amount varies as we change from KCl to KBr, or, in other words, that the negative ion has an effect. This is quite apart from the difficulty of accounting for the sign of the potential difference. I do not see that the relative solubilities of mercurous chloride and bromide can be used to help out matters, because we do not have a saturated solution at all, and the difference in the electromotive forces is more likely to be connected with the difference of solubility as cause than as effect.

There are no experimental data, so far as I know, on potential differences at the contact surface of reversible electrodes except some measurements by Neumann,[3] and these do not establish the point they were intended to prove owing to an unfortunate choice of solutions. He measured the potential difference between thallium and solutions of thallium salts. Most of the salts were salts of organic acids, and Ostwald[4] had already found that when

[1] This will not hold true till the concentration of the salt becomes zero; else we should get in all cases the same potential difference, that of the metal against pure water, which is not true. There will certainly be a minimum concentration beyond which the dissolved substance will not have the properties of matter in mass, and the potential difference will then be a function of the concentration.

[2] Zeitschr f. ph. Chem., 12, 295, 1893, Table V.

[3] Ibid., 14, 225, 1894.

[4] Ibid., 1, 605, 1887,

the negative ion was an organic radical its nature was immaterial. To settle this question one should take negative ions which show marked differences with non-reversible electrodes, such as chlorides, bromides, and iodides. As the negative ion has a very marked influence in these last-named cases, and as there is no reason to suppose that the haloid salts form a class by themselves, the simplest assumption is that the negative ion always has an effect, and that in the cases in which this does not appear, such as the organic radicals, we are measuring something else which is the same in all the cases. Le Blanc[1] found something similar in his studies on polarization, where, beyond a certain point, he obtained the value for the primary decomposition of water.

There are certain quantitative relations connected with the change of the negative ion which deserve to be brought out, and in Table IV. are given the most probable values for the potential

TABLE IV.

| Solution. | Zn\|Sol | Cd\|Sol | Sol\|Hg |
|---|---|---|---|
| Chlorides | 0.589 | 0.255 | 0.562 |
| Bromides | 0.507 | 0.174 | 0.483 |
| Iodides | 0.436 | 0.104 | 0.410 |

differences of the metals Hg, Zn, and Cd in solutions of chlorides, bromides, and iodides; while in Table V. are the corresponding

TABLE V.

| Solution. | Zn\|Sol\|Hg | Cd\|Sol\|Hg |
|---|---|---|
| Chlorides | 1.151 | 0.817 |
| Bromides | 0.990 | 0.657 |
| Iodides | 0.846 | 0.514 |
| Sulfates | 1.302 | 0.969 |

[1] Zeitschr. f. ph. Chem., 8, 315, 1891.

values for the single-liquid non-reversible cells with Zn and Hg, Cd and Hg as electrodes.[1]

We notice that the numerical change in passing from a chloride to a bromide or iodide solution is the same for these three metals and that the sign is the same for zinc and cadmium as is shown in Table VI. This enables us to formulate matters a little more

TABLE VI.

| Solution. | Zn | Cd | Hg |
|---|---|---|---|
| KCl−KBr . . . . . | 0.082 | 0.081 | −0.079 |
| KBr−KI . . . . . | 0.071 | 0.070 | −0.073 |
| KCl−KI. . . . . | 0.153 | 0.150 | −0.152 |

clearly. The potential difference between a metal and a salt solution is the sum of two terms, one due to the metal and the solvent, the other to the negative ion. For certain metals in certain solutions, the term due to the negative ion is independent, numerically, of the nature of the metal considered. For instance, the potential difference Zn|KCl, Zn|KBr, Cd|KCl, Cd|KBr, Hg|KCl, and Hg|KBr will be $A+a$, $A+b$, $B+a$, $B+b$, $C-a$, and $C-b$. The electromotive forces of the cells Zn|KCl|Cd and Zn|KBr|Cd will be $E_1=A+a-B-a$ and $E_2=A+b-B-b$, whence we see that $E_1=E_2$, which had already been found experimentally. For Zn|KCl|Hg and Zn|KBr|Hg we shall have $E_1=A+a-C+a$ and $E_2=A+b-C+b$, and $E_1$ will not be equal to $E_2$. By means of the data in my first paper on this subject,[2] we can now extend our generalization and make it more precise. With the metals, Mg, Zn, Cd, Sn, Pb, and Bi in solutions of chlorides, bromides, iodides, sulfates, nitrates, acetates, carbonates, and oxalates, the term due to the negative ion is not a function of the electrode. There is not much doubt but that the alkaline metals, the metals of the alkaline earths, and the metals of the iron group belong in this

[1] There is certainly an error in the relative positions of Sn and Pb as shown by my determinations, and I do not therefore give any data for them in Table V.

[2] Zeitschr. f. ph. Chem., 12, 294, 1893, Table III.

series. Oswald's measurements show that most organic acids may be added to the above list of solutions. With mercury the numerical value of the term due to the negative ion is the same as with the previous metals, but the sign is opposite. With platinum the numerical value is no longer the same. In which of these three groups copper, silver, gold, and the other metals belong I cannot say, though silver is probably like mercury. The results in Tables IV.–VI. open up a whole series of problems to be settled by future investigators. The values for the differences of the terms for any two negative ions have to be determined with accuracy; the behavior of the metals Cu, Ag, etc., must be examined. The work of Magnanini[1] shows that other relations hold when the dissolved salt is an oxidizing or reducing agent, and that the value Zn|RX|Cd, for instance, is independent of the metals only when RX is not an oxidizing agent. It is also well known that in cases where the electrode metal cannot exist in the solution as ion, the general relations already pointed out do not hold. From the results of Negbaur[2] and of Jones[3] we must conclude that the term which I have represented by *A*, *B*, *C*, etc., varies with the nature of the solvent. The amount of this variation is entirely unknown as yet, and it is equally impossible to say beforehand how a change in the solvent will affect the term due to the negative ion.

If we consider the cell $Zn|ZnCl_2|ZnBr_2|Zn$, the two solutions being assumed to be of the same concentration and dissociation and the wandering velocity of the bromine ion being further assumed to be identical with that of the chlorine ion, we should expect an electromotive force of 0.080 volts. This has not been taken into account by Goodwin[4] in his determinations of the solubilities of silver chloride, bromide, and iodide. Goodwin determined the electromotive force of the cells

$$Ag|AgNO_3|AgCl + KCl|Ag,\ Ag|AgNO_3|AgBr + KBr|Ag,\ Ag|AgNO_3|AgI + KI|Ag.$$

[1] Rend. Acc. Line., 6, 182, 1890. [2] Wied. Ann., 47, 27, 1892.

[3] Zeitschr. f. ph. Chem., 14, 346, 1894.

[4] Ibid., 13, 645, 1894. It is only fair to Mr. Goodwin and to myself to say that I have pointed out to him privately the objections I made to his results in order that he might correct them himself if he felt so inclined. He thinks, however, that it would be better for me to make my comments in print, and I have accordingly done so.

From the observed electromotive forces the solubilities were calculated by the formula $S = \sqrt{\frac{p_1 p_2}{\phi}}$, where $\log \phi = \frac{E}{C}$. In this equation $s$ is the solubility, $p_1$ the concentration of the Ag ions in the nitrate solutions, $p_2$ the concentration of the Cl, Br, or I ions in the corresponding solutions, $E$ is the electromotive force of the cells, and $C$ the integration constant which is equal at 25° to 0.0256. It is more than probable that a correction should be applied for a possible difference of $\log P$ in nitrate and chloride solutions, but as this value is not accurately determined, I will first calculate the solubilities on the assumption that $\log P_{NO_3} = \log P_{Cl}$.[1] We find from Table VI. $\log P_{Cl} - \log P_{Br} = 0.080$ and $\log P_{Cl} - \log P_{I} = 0.152$ volts. These values are to be subtracted from the electromotive forces observed in the cells with AgBr and AgI, in order to get the term $E$ called for by the formula. In Tables VII.–IX. I give the results of these calculations. In the first column are the values for $p_1$; in the second those for $p_2$; in the third the observed electromotive forces; in the fourth the solubilities as calculated by Goodwin; in the fifth the solubilities as calculated by myself under the assumption that $\log P_{NO_3} = \log P_{Cl}$; and in the sixth the values if one assumes further that $\log P_{NO_3} - \log P_{Cl} = 0.03$ volts. I also give the solubilities found by Kohlrausch and Rose,[2] and by Holleman[3] with the conductivity method.

It will be seen that the second column of solubilities agrees much better with the results obtained by other investigators than the solubilities calculated by Goodwin. The solubilities in the last column do not show so good an agreement; but I do not feel sure that this proves that the formula by which they are calculated is wrong. It seems to me quite as probable that these figures represent the actual solubilities in the cells examined by Goodwin, but not the real solubilities of AgCl, AgBr, AgI. The solubilities of AgCl and AgBr are much changed by contin-

[1] I use the term $\log P_{Cl}$ to denote the value of $\log P$ for a given metal when in a chloride solution. $\log P_M$ denotes $\log P$ for the metal $M$ without reference to any particular solution, and is a purely abstract conception having no numerical value as yet.

[2] Zeitschr. f. ph. Chem., 12, 324, 1893. [3] Ibid., 12, 125, 1893.

TABLE VII.[1]

| Conc. Ag ions = $p_1$. | Conc. Cl ions = $p_2$. | E.M.F. | Calc. $S_1$ | Calc. $S_2$ | Calc. $S_3$ |
|---|---|---|---|---|---|
| 0.0813 | 0.0861 | 0.451 | $1.24 \times 10^{-5}$ | $1.25 \times 10^{-5}$ | $2.25 \times 10^{-5}$ |
| 0.0813 | 0.0861 | 0.449 | $1.28 \times 10^{-5}$ | $1.30 \times 10^{-5}$ | $2.34 \times 10^{-5}$ |
| 0.04295 | 0.04455 | 0.418 | $1.25 \times 10^{-5}$ | $1.25 \times 10^{-5}$ | $2.24 \times 10^{-5}$ |
| 0.04295 | 0.04455 | 0.419 | $1.23 \times 10^{-5}$ | $1.22 \times 10^{-5}$ | $2.20 \times 10^{-5}$ |
| Solubility. AgCl at 25° Average . . | | | $1.25 \times 10^{-5}$ | $1.25 \times 10^{-5}$ | $2.26 \times 10^{-5}$ |
| Kohlrausch & Rose . . . . . | | | $1.44 \times 10^{-5}$ | at 25° | |
| Holleman . . . . . | | | $1.81 \times 10^{-6}$ | at 25° | |

TABLE VIII.

| Conc. Ag ions = $p_1$. | Conc. Br ions = $p_2$. | E.M.F. | Calc. $S_1$ | Calc. $S_2$ | Calc. $S_3$ |
|---|---|---|---|---|---|
| 0.0813 | 0.0861 | 0.598 | $7.1 \times 10^{-7}$ | $33.8 \times 10^{-7}$ | $60.7 \times 10^{-7}$ |
| 0.0813 | 0.0861 | 0.603 | $6.4 \times 10^{-7}$ | $30.1 \times 10^{-7}$ | $55.0 \times 10^{-7}$ |
| 0.0813 | 0.0861 | 0.597 | $7.2 \times 10^{-7}$ | $34.4 \times 10^{-7}$ | $61.9 \times 10^{-7}$ |
| 0.04295 | 0.04455 | 0.570 | $6.4 \times 10^{-7}$ | $30.5 \times 10^{-7}$ | $54.9 \times 10^{-7}$ |
| 0.04295 | 0.04455 | 0.571 | $6.3 \times 10^{-7}$ | $29.9 \times 10^{-7}$ | $53.8 \times 10^{-7}$ |
| 0.04295 | 0.04455 | 0.570 | $6.4 \times 10^{-7}$ | $30.5 \times 10^{-7}$ | $54.9 \times 10^{-7}$ |
| Solubility. AgBr at 25° Average . . | | | $6.6 \times 10^{-7}$ | $31.5 \times 10^{-7}$ | $56.9 \times 10^{-7}$ |
| Kohlrausch & Rose . . . . . | | | $20.9 \times 10^{-7}$ | at 25° | |
| Holleman . . . . . | | | $30.2 \times 10^{-7}$ | at 25° | |

TABLE IX.

| Conc. Ag ions = $p_1$. | Conc. I ions = $p_2$. | E.M.F. | Calc. $S_1$ | Calc. $S_2$ | Calc. $S_3$ |
|---|---|---|---|---|---|
| 0.0813 | 0.0861 | 0.815 | $1.02 \times 10^{-8}$ | $19.9 \times 10^{-8}$ | $35.7 \times 10^{-8}$ |
| 0.0813 | 0.0861 | 0.813 | $1.06 \times 10^{-8}$ | $20.7 \times 10^{-8}$ | $37.2 \times 10^{-8}$ |
| 0.0813 | 0.0861 | 0.815 | $1.02 \times 10^{-8}$ | $19.9 \times 10^{-8}$ | $35.7 \times 10^{-8}$ |
| 0.04295 | 0.04455 | 0.787 | $0.94 \times 10^{-8}$ | $18.0 \times 10^{-8}$ | $32.3 \times 10^{-8}$ |
| 0.04295 | 0.04455 | 0.786 | $0.96 \times 10^{-8}$ | $18.3 \times 10^{-8}$ | $32.9 \times 10^{-8}$ |
| 0.04295 | 0.04455 | 0.790 | $0.88 \times 10^{-8}$ | $17.0 \times 10^{-8}$ | $30.5 \times 10^{-8}$ |
| Solubility. AgI at 25° Average . . | | | $0.98 \times 10^{-8}$ | $19.0 \times 10^{-8}$ | $34.0 \times 10^{-8}$ |
| Kohlrausch & Rose . . . . . | | | $60.00 \times 10^{-8}$ | at 18°.0 | |
| Holleman . . . . . | | | $395.00 \times 10^{-8}$ | at 28°.4 | |

[1] $S_1$ and $S_2$ in this table should be identical, as they are calculated from the same data by the same formula; the variations are due to errors in calculation.

ued shaking,[1] and I cannot find that Goodwin has taken this into account at all. I conclude, therefore, that if he had shaken his AgCl and AgBr, he would have found much smaller electromotive forces than those recorded in his paper. He has tried to prove the accuracy of his formula in two ways. Having calculated the solubilities by substituting the experimental data for the electromotive forces in the formula, he reverses the operation, and substituting the solubilities he calculates the electromotive forces. It is true that there is an intervening step, but the principle is the same, also the result. If he had taken the cells

$Ag|AgNO_3|AgCl + KCl|Ag$ and $Ag|AgNO_3|AgBr + KBr|Ag$

and substituted directly in these the fallacy of such a test would have been patent. Instead of this he has combined the two cells

$$Ag|AgCl+KCl|AgNO_3|Ag|AgNO_3|AgBr+KBr|Ag = Ag|AgCl+KCl|AgBr+KBr|Ag,$$

calculated the electromotive force of the resultant cell, and compared this with the experimental value and with the difference of the mean of the two component cells. Any other formula, which had given fairly constant values for the solubilities, would have stood the test equally satisfactorily. If, instead of taking Goodwin's formula and his value for AgBr, $6.6 \times 10^{-7}$ reacting weights per liter, one takes, for instance, my first modification of his formula and the corresponding value for AgBr, $31.5 \times 10^{-7}$ units, one will reproduce his table exactly. One cannot agree with him when he says in regard to this table:[1] "Die Uebereinstimmung der beobachteten mit der berechneten Werten ist eine sehr gute, wie sie ja nicht anders sein konnte, wenn die frühere Formel (25), nach der die Löslichkeiten berechnet wurden, überhaupt richtig war. Sie bestätigt also diese Formel." The other proof is not satisfactory in the light of my experiments. Goodwin determined the solubility of thallium bromide by the electrical and by the analytical methods, the difference between the two being about 10 per cent of the total solubility. This result cannot be compared with the experiments on the solubilities of the silver haloids, because the conditions were not the same.

[1] Proc. of Am. Acad., 30, 325, 1894. [2] Zeitschr. f. ph. Chem., 13, 651, 1894.

In the thallium determinations the cell used was of the form $Tl|TlBr+KNO_3|TlBr+KBr|Tl$. There were bromine ions in contact with both electrodes, while with the silver salts the bromine ions came in contact with one electrode.

One other point remains to be considered, whether the potential difference at the surface of a reversible electrode is a function of the concentration at all. The only direct measurements are those of Neumann,[1] which confirm the Nernst theory in every detail. In addition, there are many determinations on two-liquid cells, made chiefly by Ostwald's pupils, and in all these cases there is a most satisfactory agreement between the theory and the facts. On the other hand, there are a few observations by other people which are not so easily reconciled with the theory. In Table X. I give some measurements of Paschen's[2] on cells having zinc and mercury electrodes, and solutions of $ZnSO_4$ and $MgSO_4$ of varying concentrations as electrolyte. The first column gives the nature of the cell; the second, the specific gravity of the electrolyte; the third, the concentration in grams per hundred grams of the solution; the fourth, the electromotive force observed. The values for the concentrations are only approximate because they were not determined by Paschen directly, and I have taken them from Landolt and Börnstein's tables.

TABLE X.

| Electrodens. | Electrolyte. | Density. | Per cent in grams. | E.M.F. |
|---|---|---|---|---|
| ZnHg | $MgSO_4$ | 1.042 | 4.0 | 1.194 |
| ZnHg | $MgSO_4$ | 1.040 | 4.0 | 1.236 |
| ZnHg | $MgSO_4$ | 1.040 | 4.0 | 1.186 |
| ZnHg | $ZnSO_4$ | 1.433 | 32.9 | 1.249 |
| ZnHg | $ZnSO_4$ | 1.409 | 31.5 | 1.252 |
| ZnHg | $ZnSO_4$ | 1.403 | 31.1 | 1.309 |
| ZnHg | $ZnSO_4$ | 1.402 | 31.1 | 1.327 |
| ZnHg | $ZnSO_4$ | 1.400 | 31.0 | 1.236 |
| ZnHg | $ZnSO_4$ | 1.315 | 25.5 | 1.310 |
| ZnHg | $ZnSO_4$ | 1.305 | 25.0 | 1.238 |

[1] Zeitschr. f. ph. Chem., 14, 225, 1894. [2] Wied. Ann., 43, 570, 1891.

These figures lose a good deal of their value owing to the considerable variation in the determinations for the same solutions, and because the range of concentrations is too limited; but two things are very noticeable in spite of this. In the cells $Zn|ZnSO_4|Hg$, the electromotive force does not decrease with increasing concentration of zinc sulfate, as it should according to the theory. The cells $Zn|MgSO_4|Hg$, have the same value as the cells $Zn|ZnSO_4|Hg$, or a smaller one, while the theory demands a larger one. The same thing is seen, though in a less satisfactory manner, in the experiments of Damien.[1] He used zinc and copper as electrodes, and his results are given in Table XI. The first

TABLE XI.

ZnCu Electrodes.

| Electrolyte. | Density at 15°. | Per cent in grams. | E.M.F. | Amalg. Zn E.M.F. |
|---|---|---|---|---|
| $K_2SO_4$ . . . . | 1.036 | 4.5 | 1.035 | 1.067 |
| $Na_2SO_4$ . . . . | 1.038 | *10.0 | 1.012 | 1.037 |
| $(H_4N)_2SO_4$ . . | 1.075 | 13.1 | 1.012 | 1.019 |
| $MgSO_4$ . . . . | 1.035 | *5.8 | 1.047 | 1.059 |
| $Al_2(SO_4)_3$ . . . | 1.135 | 5.8 | 1.050 | 1.062 |
| $ZnSO_4$ . . . . | 1.064 | *9.2 | 1.004 | 1.047 |
| KCl . . . . . | 1.077 | 12.0 | 0.788 | 0.802 |
| NaCl . . . . | 1.061 | 8.5 | 0.805 | 0.810 |
| $NH_4Cl$ . . . . | 1.039 | 13.0 | 0.845 | 0.850 |
| $BaCl_2$ . . . . | 1.110 | 12.0 | 0.782 | 0.820 |
| $CaCl_2$ . . . . | 1.212 | 23.0 | 0.743 | 0.751 |
| $ZnCl_2$ . . . . | 1.384 | 37.5 | 0.746 | 0.752 |

Values with a * refer to hydrated salt.

column shows the electrolyte; the second, the specific gravity of the solution; the third, the percentage composition; the fourth, the electromotive force when ordinary zinc was used; the fifth, the corresponding values when the electrode was amalgamated.

As will be noticed, there are marked variations even in cases where no one claims that there should be any, such as between

[1] Ann. chim. phys. (6), 6, 289, 1885. The reference to Vol. V. in Wied. Elektrizität I, 734, also in Beibl. 10, 185, is a misprint.

ammonium sulfate and potassium sulfate solutions, between calcium chloride and ammonium chloride. This weakens the conclusions which one would like to draw from these experiments; but, making allowance for a large experimental error, it is still very curious that $Zn|ZnSO_4|Hg$ should give so nearly the same value as the cells with indifferent sulfates, and that zinc chloride should be indistinguishable electrically from calcium chloride. The experiments of Hockin and Taylor[1] may be interpreted either way. They found that the combination of zinc and another metal in sulfuric acid gave a higher electromotive force than the same two metals in a saturated solution of zinc sulfate. This is not so convincing as if they had used potassium sulfate instead of sulfuric acid, because in all except dilute solutions free acids do give a higher value than the corresponding salts. The reason for this variation is unknown. When it comes to the absolute values in the zinc sulfate solution, matters are no better. In some of the metals, notably cadmium and mercury, the zinc sulfate appears to give the same value as any other sulfate; with others there is a qualitative agreement with Nernst's theory. The same remarks hold true of the work of Lindeck.[2] I have not access to the original paper of Wolff, and the review of it[3] is two meager to be of much assistance. He investigated, among other things, the effect of changing the concentration of the zinc sulfate in a one-liquid cell. His results are given in Table XII. The first column

Table XII.

| | Density. | E.M.F. |
|---|---|---|
| $Zn\|ZnSO_4\|Cu$ . . . . . | 1.438–1.001 | 0.965–1.066 |
| $Zn\|ZnSO_4\|CuO$ . . . . . | 1.427–1.003 | 1.008–1.015 |
| $Zn\|ZnSO_4\|Fe$ . . . . . | 1.427–1.003 | 0.378–0.385 |
| $Zn\|ZnSO_4\|Pb$ . . . . . | 1.427–1.003 | 0.456–0.587 |
| $Zn\|ZnCl_2\|Cu$ . . . . . | 1.637–1.003 | 0.734–0.930 |
| $Zn\|ZnCl_2\|Fe$ . . . . . | 1.917–1.003 | 0.385–0.390 |
| $Zn\|Zn(NO_3)_2\|Cu$ . . . . . | 1.496–1.004 | 0.669–0.698 |

[1] J. Tel. Eng., 8, 282, 1879. [2] Wied. Ann., 35, 311, 1888.
[3] Beibl., 12, 700, 1888.

shows the electrodes and the electrolyte; the second, the concentrations of the latter in specific gravities; the third, the corresponding electromotive forces.

In all cases there is a qualitative agreement with the theory; that is, the electromotive force increases with decreasing concentration of zinc sulfate. The quantitative agreement is not so satisfactory. In the second, third, sixth and last cells given in the table the variations are much too small; while, in the other cases, they are too large. The ratio of the strongest solutions to the weakest in the experiments of Wolff lies between 100 and 1000 to 1, which corresponds to a change of electromotive force of 0.05–9 volts owing to the bivalence of zinc. Some experiments which I made with the cell $Cd|CdCl_2|Hg$, the strength of the solution being unknown, gave me 0.815, 0.821, 0.814, average 0.817 volts, the same value which I had already found for the KCl solution.

The simplest way to decide what effect the concentration of the reversible ion, if I may use such a phrase, has on the electromotive force would be to make a series of measurements on reversible electrodes by the dropping-mercury method. I have not been in a position to do this, and I have had to find an easier, though less satisfactory manner of settling the question. Suppose we have electrodes of zinc and copper in a mixture of zinc and copper sulfates, one solution. Increasing the concentration of the zinc sulfate or decreasing the concentration of the copper sulfate must diminish the electromotive force of the cell, and *vice versa* if the reverse operations be performed. Through the courtesy of Professors Trowbridge and Peirce of the Physical Laboratory, I have been able to make the few experiments necessary. As it was only required to find out whether there was any change at all, there was no need of determining the absolute value of the electromotive force. This made the experimental part very easy. I connected the cell with a large external resistance and a galvanometer. I changed the ratio of the two components in the solution and noted the position of the galvanometer needle. I made measurements with the electrodes in pure zinc sulfate solutions, in pure copper sulfate solutions, and in mixtures of these in varying proportions. Under all these different conditions I obtained the

same electromotive force, showing that it is a function neither of the relative nor of the absolute concentrations.[1] Although one obtains the same value from the different solutions, they do not behave exactly alike. With solutions of pure copper sulfate or with mixtures containing copper sulfate in any quantity, the maximum value is obtained at once and is very constant. With solutions of pure zinc sulfate or mixtures containing only traces of copper sulfate, the maximum value can be obtained only by vigorous stirring and is very inconstant. There is, of course, nothing surprising about this, as it is what one would have predicted. It is a very curious fact that the Nernst formula, though deduced from apparently erroneous assumptions, should yet give the effect of changes of concentration in a two-liquid cell with such surprising accuracy.

It will be noticed that the electromotive forces of the non-reversible cells have nothing to do with the heats of reaction. This has always been known; but it acquires a new significance, since it has been shown that the non-reversible cells are to be considered, as far as the electromotive forces are concerned, as limiting cases of the reversible two-liquid cells. In the cell $Zn|H_2SO_4|Ag$ there is not much doubt what reaction takes place; but it has nothing to do with determining the electromotive force. An interesting example of this, which also brings up another point, is the cell $Cu|CuSO_4|Pt$. Here the reaction consists in the replacement of copper by copper. What happens experimentally, on closing the circuit, is that copper is dissolved from the copper electrode and precipitated on the platinum until the latter becomes, electrically considered, an electrode of pure copper, when further action becomes impossible.[2] Overbeck[3] made some experiments a few years ago to determine what thickness of copper made a platinum electrode behave like a piece of pure copper. His

[1] This applies only to electrodes reversible in respect to the kation. I hope to treat the case of electrodes reversible in respect to the anion in another paper.

Since this paper was written I have seen the article of J. Meyer, Wied. Ann., 53, 898, 1894, which confirms my views, though with certain exceptions.

[2] When I performed this experiment I was not aware that a similar one had been described by Gladstone and Tribe, Proc. Roy. Soc., 1876.

[3] Wied. Ann., 31, 337, 1887.

method was to deposit copper on platinum electrolytically, and was open to the objection that it was almost impossible to be certain that the copper was deposited uniformly over the surface of the platinum. By using the cell $Cu|CuSO_4|Pt$, it would seem that this difficulty might be avoided, as the plating is stopped automatically as soon as the minimum thickness is reached. Suppose we balance this cell to some extent by an electromotive force less than its own. There will still be a tendency for copper to be deposited on the platinum; but it cannot be deposited to the thickness corresponding to pure copper, as it must then dissolve up again under the influence of the external electromotive force. It can precipitate only till equilibrium is reached, and we shall have the condition referred to by Gibbs,[1] of a substance present in too small quantities to have the properties of "matter in mass." By making the external electromotive force differ infinitely little from the electromotive force of the cell, it would be possible, theoretically at any rate, to obtain an infinitely thin film of copper. It is to the separation of the ion on the electrode in such small quantities as not to have the properties of matter in mass that is due the gradual change of the polarization instead of having a sudden jump from the initial to the final value.

The main results of this research may be summed up as follows:

1. The potential difference between a metal and an electrolyte is not a function of the concentration of the salt solution nor of the nature of the positive ion except in certain special cases.

2. It is a function of the electrode, of the negative ion, and of the solvent.

3. In aqueous solutions, the potential difference is the sum of the term due to the electrode and the term due to the negative ion in the normal cases.

4. For most metals in most electrolytes the term due to the negative ion has the same numerical value and the same sign.

5. For mercury it has the same numerical value, but the opposite sign; for platinum, neither the same numerical value nor the same sign.

CAMBRIDGE, December, 1895.

[1] Thermodynamische Studien, p. 393.

# ON THE FREEZING-POINTS OF DILUTE AQUEOUS SOLUTIONS.

BY E. H. LOOMIS.

TWO years ago I submitted a series of freezing-points of dilute aqueous solutions.[1] After a year of unavoidable interruption the work was resumed, and the new results form the material of the present paper.

The method has remained entirely unchanged and is fully described in the former papers.

The only change in the apparatus was the enlargement of the "freezing-tube," so that it now receives 200 cc. of the solution instead of 70 cc. as before. It was thought that this change would eliminate a possible source of error which might have come from the "sensitiveness" of the smaller quantity of the solution to external temperatures. No reduction, however, of the experimental error has resulted from this change.

The thermometer was the same instrument used in the former observations. The work was done in a basement room of the John C. Green School of Science Building. Here it was possible to avoid serious temperature changes during the entire day. The temperature was kept as near 0° C. as possible, and maintained fairly constant by means of the strong draught of a ventilation shaft opening into the room. By regulating the admission of cold air at the window, the temperature changes were kept within the limits of 1–2 degrees. It is much to be regretted that this work could not be done at the constant temperature of 0° C. A degree of accuracy could thus be reached, I think, which is otherwise unattainable.

The thermometer was kept throughout the entire period of the observations within about 1° C. of the freezing-point.

Attention may be called to four points in regard to the method.

[1] Physical Review, Vol. I., 1893, pp. 199 and 274.

1. The freezing-point is determined with so slight traces of ice present that no correction for change of concentration in the solution is necessary. (The overcooling is but 0°.15 C.) I am not aware that the value of this correction so generally applied in other methods has been experimentally determined, and since it not infrequently amounts to 10 per cent of the entire observed depression it may perhaps be dangerous to apply it without some experimental justification.

2. The method eliminates all possibility that the observer's bias may affect the results.

3. The reading of the thermometer is made with the mercury column absolutely stationary during 1–2 minutes.

4. The solution to be examined, as well as the water in which the zero point of the thermometer is determined, is surrounded by a medium which is but 0°.3 C. below its own freezing-point, and is further carefully insulated from this by two glass walls and the air layer between them. Thus the solution and its "ice" are able to come to their equilibrium temperature in as nearly an adiabatic condition as possible.

It may be said that as soon as this last feature of the method suggested itself I employed, as was natural, a bath whose temperature was *exactly* that of the freezing-point to be determined, but it was soon found that the observed freezing-points were too high (Nernst's convergence temperature), and the temperature difference of 0°.3 C. was finally chosen, since it was found that this reduced the "convergence temperature" to the actual freezing-point sought. The method by which this was ascertained was by observing at what temperature of the bath the freezing-points of water, obtained with only slight traces of ice in the water, agreed with those obtained with large quantities of ice present.[1]

The vast theoretical importance of these freezing-points has occasioned much very careful work in this field during the past few years, and many questions have arisen in regard to the various methods thus developed. Some of the more important of these questions will be considered in a subsequent paper.[2]

The present series of observations comprises the following compounds, all of which are electrolytes: —

[1] Physical Review, Vol. I., p. 213. [2] p. 293.

TABLE I.

| 1 Compound. | 2 $m$ | 3 Grams per liter solution at 18° C. | 4 Specific gravity, $\frac{18°}{4°}$ | 5 Electrical conductivity,[1] $k \cdot 10^6$, 18° C. | 6 Specific gravity solution, $m = 0.20$, $\frac{18°}{4°}$. | 7 Firm name. | 8 Standard solution prepared. |
|---|---|---|---|---|---|---|---|
| KCl | 1 | 74.59 | 1.0450 | 919 | 1.0082 | Eimer & Amend. | By direct weight. |
| $NH_4Cl$ | 1 | 53.49 | 1.0152 | 909 | 1.0018 | Eimer & Amend. | By direct weight. |
| $BaCl_2$ | ½ | 103.95 | 1.0889 | 655 | 1.0352 | Merck & Co. | Gerlach's Tables.[2] |
| MgCl | ½ | 47.63 | 1.0381 | $m=0.20$ [4] 290 | 1.0148 | Eimer & Amend. | Kohlrausch's Tables.[3] |
| HCl | 1 | 35.45 | 1.0166 | 2794 | 1.0024 | Eimer & Amend. | Kohlrausch's Tables.[5] |
| $K_2SO_2$ | ½ | 87.17 | 1.0662 | $m=0.20$ 304 | 1.0262 | Eimer & Amend. | Direct weight. |
| $Na_2SO_4$ | ½ | 71.09 | 1.0606 | 474 | 1.0239 | Eimer & Amend. | Direct weight. |
| $K_2CO_3$ | ½ | 69.14 | 1.0578 | 660 | 1.0231 | Trommsdorff. | Direct weight. |
| $Na_2CO_3$ | ½ | 53.06 | 1.0518 | Standard | 1.0206 | Prepared in Lab. | Direct weight. |
| $KNO_3$ | 1 | 101.18 | 1.0603 | 752 | 1.0114 | Trommsdorff. | Direct weight. |
| $NaNO_3$ | 1 | 85.10 | 1.0546 | 615 | 1.0102 | Trommsdorff. | Direct weight. |
| $NH_4NO_3$ | 1 | 80.09 | 1.0309 | 831 | 1.0053 | Trommsdorff. | Direct weight. |
| $H_3PO_4$ | ⅓ | 32.67 | 1.0166 | 209 | 1.0096 | Trommsdorff. | Hullet's Titration. |

[1] In "mercury units."

[2] Hoffmann's Tabellen, Berlin, 1877, p. 121.

[3] Wiede. Ann., Bd. VI., 1879, p. 38.

[4] Solution $m=\frac{1}{2}$ accidentally thrown away before $k$ was determined.

[5] Leitfaden d. Physik, 1892, p. 403.

In the foregoing table, and elsewhere throughout the present paper, $m$ denotes the *gram-molecular* concentration of the solution; that is, $m=1$, for example, indicates that a liter of the *solution* contains as many grams of the compound as there are units in its molecular weight. Columns 4 and 5 give respectively the specific gravity $\left(\frac{18^\circ}{4^\circ}\right)$, and electrical conductivity of the standard solutions whose respective concentrations are found in column (2). In addition, for the sake of ready reference, the table gives the specific gravity of the solutions for the molecular concentration, $m=0.20$, and further the name of the makers from whom the compound was obtained. In the last column is given the manner in which the solution was prepared.

*Solutions.*

The solutions which were prepared by direct weighing were made from carefully recrystallized salts. The drying was accomplished as thoroughly as the nature of the salt would permit in accordance with the prescribed methods.

The solution, $H_3PO_4$, $m=\frac{1}{3}$, was prepared for me by Mr. Hullet of the Princeton Chemical Laboratory, and I wish here to thank him for the careful manner in which the titration and subsequent analysis were performed by him.

In every case the specific gravity and electrical conductivity of the standard solutions were determined in order to control their accuracy. I cannot agree with Mr. Jones,[1] who appears to be of the opinion that the specific gravity and conductivity of a supposedly standard solution can furnish no conclusion in regard to its accuracy.

In fact, there seems to be no reason to believe that a normal solution made from carefully prepared salts, in accordance with accepted tables of specific gravity, and found to have the exact specific gravity and electric conductivity corresponding to such a solution should not be "pure," at least within the limits of accuracy yet reached in the present methods of making freezing-point observations. I think it cannot be too strongly urged that in all

[1] Weide. Ann., Bd. 53, 1894, p. 394.

such work both these constants be determined, not more for the sake of the easy control which they furnish, than for the convenient comparison with others' results, which these data in regard to a solution permit.

By comparing the results in Table I. with those of Kohlrausch[1] it is found that sufficient agreement exists except in the case of HCl. This solution was titrated by Mr. Hullet from acid found to be free from the impurities likely to be present in it. The standard solution against which it was balanced, was a normal $Na_2CO_3$. The $Na_2CO_3$ was made from Trommsdorff's c. p. $NaHCO_3$ by glowing to constant weight. The specific gravity of this solution is given in the foregoing table.

The electrical conductivity was measured according to the familiar method of Kohlrausch. The "Resistance Capacity" of the electrolytic cell employed was found in the usual manner by assuming Kohlrausch's values for the conductivity of NaCl and $Na_2CO_3$.

*Determination of Specific Gravity.*

The specific gravity was determined by using a modified form of Sprengel picnometer, whose volume at 18° C. was 51.3232 c.c.

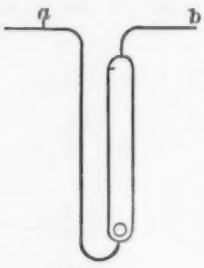

Fig. 1.

At (*a*) the glass tube is constricted to a bore of 1 mm., and at this point a fine mark is etched around the tube. At (*b*) the tube is reduced to a point, whose opening is less than 1 mm., so that the greater capillary attraction at this point over that at (*a*) may hold the liquid always at (*b*), and thus permit changes of volume in the liquid contents to be observed at (*a*). The body of the picnometer is further provided with a small glass ball. This provides for the easy displacement of air bubbles, which sometimes form on the inside walls. It is found, however, that these bubbles do not form, if one takes the precaution to keep the picnometer when not in use always supplied with water, so that its walls may not become dry. This seems to indicate that the source of these troublesome air bubbles is not

[1] Leitfaden d. Physik, Leipzig, 1892, p. 404.

the air dissolved in the solutions, but the air "condensed" on the dry walls of the glass itself.

The picnometer is filled and placed in a water bath whose temperature is kept at 18° C. ± 0°.05. The solutions were usually about 20° C. when introduced into the picnometer, and thus when placed in the colder bath the liquid in the arm (*a*) would shrink back toward the body of the picnometer, rapidly at first, and slowly at last, as its temperature became more nearly equal to that of the bath. Liquid is added at the point (*b*) as may be needed from time to time, by touching it with a glass rod or stopper moistened with the solution. When the liquid column remains stationary at (*a*), 1–2 minutes, it is known that the solution in the picnometer has the same temperature as the bath, 18° C.

*Experiment showed that whether the solution was initially at temperatures below or above 18° C., the same result was obtained, so far at least as would affect the fifth place of decimals.*

It is to be noted that three entire series of freezing-point observations, KHO, NaHO, and $HNO_3$, had to be rejected, since their specific gravity and electrical conductivity were found to be at such variance with the Kohlrausch values as to indicate some marked impurity. At the earliest opportunity I hope to determine the specific gravity and electrical conductivity of normal solutions of these compounds, together with HCl, using the utmost care in preparation of the material, and shall then measure their respective freezing-points.

The distilled water used throughout the present work had an electrical conductivity $8.10^{-10}$.

*Results.*

The following tables present the experimental results. — In column (2) is given the molecular concentration ($m$) of the solution, in (3) the observed depression of the freezing-point ($\Delta$), and in (4) is found the molecular depression $\left(\frac{\Delta}{m}\right)$. This is the value of the molecular depression as reckoned by Arrhenius. Raoult and others reckon with gram-molecules *per* 1000 *grams of water*, instead of 1 *liter of solution*. In order to compute this

TABLE II.

| 1 Compound. | 2 Gram-molecule per liter solution, $m$. | 3 Depression of freezing-point, $\Delta$. | 4 Molecular depression of freezing-point, $\frac{\Delta}{m}$. | 5 Theoretical value of $\frac{\Delta}{m}$. | 6 Theoretical value of $\Delta$. | 7 Difference. $\Delta_{th}-\Delta_{exp}$. | 8 Difference. $\Delta_{th}-\Delta_{exp}$ in per cents of $\Delta_{exp}$. |
|---|---|---|---|---|---|---|---|
| KCL | 0.01 | 0.0360° | 3.60 | 3.65 | 0.0365° | +0.0005 | +1.3 |
| | 0.02 | 0.0709 | 3.55 | 3.62 | 0.0724 | +0.0015 | +2.1 |
| | 0.03 | 0.1055 | 3.52 | — | — | — | — |
| | 0.035 | 0.1235 | 3.53 | — | — | — | — |
| | 0.05 | 0.1749 | 3.50 | 3.56 | 0.1780 | +0.0031 | +1.7 |
| | 0.10 | 0.3445 | 3.445 | 3.498 | 0.3498 | +0.0053 | +1.5 |
| | 0.20 | 0.6808 | 3.404 | 3.441 | 0.6882 | +0.0074 | +1.1 |
| | 0.40 | 1.3411 | 3.353 | — | — | — | — |
| $NH_4Cl$ | 0.01 | 0.0356 | 3.56 | 3.67 | 0.0367 | +0.0011 | +3.2 |
| | 0.02 | 0.0711 | 3.56 | (3.64) | (0.0728) | +0.0017 | +2.3 |
| | 0.035 | 0.1224 | 3.50 | — | — | — | — |
| | 0.05 | 0.1740 | 3.48 | 3.58 | 0.1790 | +0.0050 | +2.8 |
| | 0.10 | 0.3434 | 3.434 | 3.515 | 0.3515 | +0.0081 | +2.4 |
| | 0.20 | 0.6792 | 3.396 | (3.470) | (0.6940) | +0.0148 | +2.2 |
| | 0.40 | 1.3573 | 3.393 | — | — | — | — |
| HCl | 0.01 | 0.0361 | 3.61 | 3.71 | 0.0371 | +0.0010 | +2.8 |
| | 0.02 | 0.0719 | 3.60 | 3.69 | 0.0738 | +0.0019 | +2.6 |
| | 0.05 | 0.1797 | 3.59 | 3.66 | 0.1830 | +0.0033 | +1.9 |
| | 0.10 | 0.3546 | 3.546 | 3.616 | 0.3616 | +0.0070 | +2.0 |
| | 0.20 | 0.7130 | 3.565 | 3.563 | 0.7126 | −0.0004 | ±0. |
| | 0.30 | 1.0837 | 3.612 | — | — | — | — |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| $BaCl_2$ | 0.01 | 0.0499 | 4.99 | (5.20) | (0.0520) | +0.0021 | +4.4 |
| | 0.02 | 0.0990 | 4.95 | (4.92) | (0.0984) | −0.0006 | −0.6 |
| | 0.05 | 0.2385 | 4.77 | 4.74 | 0.2370 | −0.0015 | −0.6 |
| | 0.10 | 0.4690 | 4.690 | (4.58) | (0.458) | −0.0110 | −2.3 |
| | 0.20 | 0.9310 | 4.655 | (4.36) | (0.872) | −0.0590 | −6.3 |
| $MgCl_2$ | 0.01 | 0.0514 | 5.14 | No data accessible. | | | |
| | 0.02 | 0.1014 | 5.07 | | | | |
| | 0.05 | 0.2489 | 4.98 | | | | |
| | 0.10 | 0.4948 | 4.948 | | | | |
| | 0.15 | 0.7444 | 4.965 | | | | |
| | 0.20 | 1.0039 | 5.019 | | | | |
| | 0.25 | 1.2699 | 5.079 | | | | |
| | 0.30 | 1.5557 | 5.186 | | | | |
| $K_2SO_4$ | 0.01 | 0.0492 | 4.92 | 4.95 | 0.0495 | +0.0003 | +0.6 |
| | 0.02 | 0.0952 | 4.76 | (4.76) | (0.0952) | ±0. | ±0.0 |
| | 0.05 | 0.2271 | 4.54 | 4.52 | 0.2260 | +0.0011 | +0.5 |
| | 0.10 | 0.4317 | 4.317 | 4.328 | 0.4328 | +0.0011 | 0.2 |
| | 0.20 | 0.8134 | 4.067 | (4.13) | (0.8260) | 0.0130 | 1.6 |
| | 0.30 | 1.1672 | 3.891 | — | — | — | — |
| $Na_2SO_4$ | 0.01 | 0.0509 | 5.09 | (4.96) | (0.0496) | −0.0013 | −2.5 |
| | 0.02 | 0.0974 | 4.87 | (4.74) | (0.0948) | −0.0026 | −2.5 |
| | 0.05 | 0.2297 | 4.59 | 4.49 | 0.2247 | −0.0050 | −2.2 |
| | 0.10 | 0.4340 | 4.340 | (4.26) | (0.4260) | −0.0080 | −1.8 |
| | 0.20 | 0.8141 | 4.071 | (3.97) | (0.7940) | −0.02 | −2.5 |
| | 0.30 | 1.1604 | 3.875 | — | — | — | — |

TABLE II. (*continued*).

| 1 Compound. | 2 Gram molecule per liter solution. $m$. | 3 Depression of freezing-point, $\Delta$. | 4 Molecular depression of freezing-point, $\frac{\Delta}{m}$ | 5 Theoretical value of $\frac{\Delta}{m}$. | 6 Theoretical value of $\Delta$. | 7 Difference. $\Delta_{th}-\Delta_{exp}$. | 8 Difference. $\Delta_{th}-\Delta_{exp}$ in per cents of $\Delta_{exp}$. | |
|---|---|---|---|---|---|---|---|---|
| | | ° | | | ° | ° | $\mu_\infty=140$. | $\mu_\infty=122$. |
| $K_2CO_3$ | 0.01 | 0.0507 | 5.07 | (4.66) | (0.0466) | −0.0041 | − 8.0 | −0.0 |
| | 0.02 | 0.0986 | 4.93 | (4.49) | (0.0898) | −0.0088 | − 9.0 | −1.2 |
| | 0.05 | 0.2356 | 4.71 | 4.27 | 0.2135 | −0.0221 | − 9.0 | −2.0 |
| | 0.10 | 0.4540 | 4.540 | (4.09) | (0.4090) | −0.0450 | −10.0 | −2.2 |
| | 0.20 | 0.8770 | 4.385 | (3.91) | (0.782) | −0.0950 | −11.0 | −3.8 |
| | | | | | | | $\mu_\infty=122$. | $\mu_\infty=104$. |
| $Na_2CO_3$ | 0.01 | 0.0507 | 5.07 | (4.54) | (0.0454) | −0.0053 | −10.0 | −3.0 |
| | 0.02 | 0.0986 | 4.93 | (4.32) | (0.0864) | −0.0122 | −12.0 | −5.0 |
| | 0.05 | 0.2321 | 4.64 | 4.03 | 0.2015 | −0.0306 | −13.0 | −6.0 |
| | 0.10 | 0.4416 | 4.416 | (3.78) | (0.3780) | −0.0640 | −15.0 | −7.0 |
| | 0.20 | 0.8339 | 4.170 | (3.55) | (0.710) | −0.1240 | −15.0 | −8.0 |
| $KNO_3$ | 0.01 | 0.0346 | 3.46 | 3.62 | 0.0362 | +0.0017 | + 4.9 | |
| | 0.02 | 0.0703 | 3.52 | (3.58) | (0.0716) | +0.0013 | + 1.8 | |
| | 0.025 | 0.0865 | 3.46 | — | — | — | — | |
| | 0.05 | 0.1705 | 3.41 | 3.50 | 0.1750 | +0.0045 | + 2.6 | |
| | 0.10 | 0.3314 | 3.314 | 3.409 | 0.3409 | +0.0095 | + 2.8 | |
| | 0.20 | 0.6388 | 3.194 | (3.31) | (0.662) | +0.023 | + 3.6 | |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| $NaNO_3$ | 0.01 | 0.0355 | 3.55 | 3.65 | 0.0365 | +0.0010 | + 2.8 |
| | 0.02 | 0.0690 | 3.45 | (3.62) | (0.0724) | +0.0034 | + 5.0 |
| | 0.025 | 0.0866 | 3.46 | — | — | — | — |
| | 0.05 | 0.1722 | 3.44 | 3.55 | 0.1775 | +.00053 | + 3.1 |
| | 0.10 | 0.3428 | 3.428 | 3.472 | 0.3472 | +0.0044 | + 1.3 |
| | 0.20 | 0.6689 | 3.345 | (3.409) | (0.6818) | +0.0129 | + 1.9 |
| [1] $NH_4NO_3$ | 0.01 | 0.0358 | 3.58 | | | | |
| | 0.02 | 0.0707 | 3.54 | | | | |
| | 0.025 | 0.0873 | 3.49 | | | | |
| | 0.05 | 0.1737 | 3.47 | | | | |
| | 0.10 | 0.3424 | 3.424 | | | | |
| | 0.20 | 0.6641 | 3.321 | | | | |
| $H_3PO_4$ | 0.01 | 0.0282 | 2.82 | | | | |
| | 0.02 | 0.0536 | 2.68 | | | | |
| | 0.05 | 0.1245 | 2.49 | | | | |
| | 0.10 | 0.2358 | 2.358 | | | | |
| | 0.20 | 0.4498 | 2.249 | | | | |

[1] It should be noted that in case of the $NH_4NO_3$ solutions more concentrated than $m = 0.05$ the rise of the thermometer after the freezing begins is *extremely* slow. The same is the case with $NH_4Cl$ though in a less marked degree. The usual sudden "jump" of the mercury when freezing begins after an overcooling of a liquid is *entirely* wanting. It may be noted also that the "ice" presents a milky appearance in sharp contrast to its crystalline appearance in other cases. The same was observed in the solutions $MgCl_2$, $m = 0.15, 0.20, 0.25, 0.30$. The observed depressions are clearly affected by this slowness of these solutions to come to the equilibrium temperature, and are thus too great. In the case of $NH_4NO_3$ $m = 0.20$ the matter was tested experimentally and it appeared that the maximum temperature was not reached in the usual interval of two minutes, but required at least five minutes, and gave at the end of that time a reading fully $0°.005$ C. higher than at the end of two minutes. No such difference was observed in case of $MgCl_2$, showing that here the maximum was reached in the customary two minutes. No corrections are applied, as the matter is not yet well enough understood.

value of the molecular depression, one needs in addition the specific gravity of the solution. This is found in Table I., column (6), from which the value of $\frac{\Delta}{m}$ in accordance with Raoult's definition is easily reckoned. The difference, however, is so slight, even in the most concentrated solution used, that there seems to be no advantage in publishing both values as was done in the former papers. Thus this difference amounts to only 1 % in the case of $NH_4NO_3$, $m=0.20$ where it is the greatest, while in $Na_2CO_3$ it vanishes altogether.

The value of the depression in column (3) is the mean of 5–9 *entirely independent* determinations, which show on the average a variation of 0°.001 C. The *largest* average variation shown in any complete series was 0°.0013 C. in the case of $BaCl_2$ (43 separate observations). The smallest average variation was 0°.0006 C. in the case of $Na_2CO_3$ (36 distinct observations). This is almost exactly the variation observed in the former work, and shows that the enlargement of the freezing-tube has not affected the sources of error.

*Graphic Representation of Results.*

The values of $\frac{\Delta}{m}$ as a function of $m$ are presented graphically in Plate I., Fig. 1. Ordinates represent values of $\frac{\Delta}{m}$, abscissas those of ($m$). To avoid confusion, the nitrates are represented by themselves in Fig. 2. The scale is the same as that before employed. Together with the new series are represented the values of NaCl and $H_2SO_4$ from the observations of 1893. To the NaCl results another has been added at $m=0.40$, and thus the course of the curve beyond $m=0.20$ is determined. The present method of representing *molecular depressions* rather than actual depressions commends itself, since it alone is able to show at a glance the general nature of the results and throw much light on the accuracy of the method. Neither of these appear when the depressions themselves are graphically represented, since on the one hand the *departures* from Blagden's law of strict proportionality between depression and concentration are so very slight compared

with the total *depressions* that they do not appear in the graphic representation of depressions. Thus even where these departures are the most marked, as, for example, in case of $Na_2CO_3$, the "curve" of total *depressions* differs so little from a straight line that it may be distinguished from a straight line only with the closest scrutiny. On the other hand, probable errors of many thousandths of a degree are scarcely noticeable in the curve of *depressions*.

The curves for the most part are determined by five observations, whose points are connected with straight lines. In the greater number of cases the experimental errors appear to be so comparatively small, that it would perhaps have been justifiable to assume a *perfect* regularity of results, and connect the points accordingly with the most probable *curve*, as was done in the former papers.

In case of $MgCl_2$, these five observations, at $m=0.01$, $m=0.02$, 0.05, 0.10, and 0.20, were so surprising that three additional ones were made, at $m=0.15$, $m=0.25$, and $m=0.30$. So too with KCl and $NH_4Cl$ an additional observation was made at $m=0.40$, to determine whether the converging curves actually crossed somewhere near $m=0.20$. It should be added that these two observations, together with that on NaCl at the same point, were made immediately after a special determination of the zero-point of the thermometer. Thus an error in the zero-point could not affect the *relative* depressions of the three salts. The same precaution was observed for the two observations on $Na_2SO_4$ and $K_2SO_4$ at $m=0.30$, so that there is no possible doubt that the members of these pairs of curves intersect in the region of $m=0.20$.

### *Discussion of Results.*

Apart from any theory it appears here as in the case of the electrolytes formerly studied: —

(1) That the molecular depression increases continuously with increase of dilution. The only exceptions are $MgCl_2$ and HCl in the region of greater concentration, each of which thus presents a *minimum* value of the molecular depression at $m=0.10$. In $MgCl_2$ this minimum is pronounced. In case of HCl it is perhaps less striking, but no less well established. It was to remove pos-

sible doubt about this minimum in HCl that the value at $m=0.30$ was determined. The position of this new point makes the existence of the minimum certain at about $m=0.10$.

I find that this same minimum in case of $MgCl_2$ appears in the results of Arrhenius,[1] although he must have looked upon it as due to exceptionally large errors, since he makes no reference to it in his discussion of results. I find also that in the case of HCl, Jones's[2] observations suggest unmistakably the presence of such a minimum, although his failure to call attention to it, particularly since he calls special attention to the *regularity* of the results,[3] would indicate that he believed it due to an error of some 0°.002 C.

(2) The curves are all more or less concave on their upper side.

(3) It now appears that the electrolytes thus far studied are sharply divided into two marked groups, the *first* made up of compounds containing univalent acid and basic radicals, NaCl, KCl, HCl, $NH_4Cl$, $KNO_3$, $NaNO_3$, $NH_4NO_3$; the *second* made up of those containing bivalent radicals, $MgCl_2$, $BaCl_2$, $MgSO_4$, $H_2SO_4$, $Na_2SO_4$, $K_2SO_4$, $Na_2CO_3$, $K_2CO_3$. These groups are distinct in two particulars, (1) in the *amount* of the molecular depression of the freezing-point, and (2) in the *rate* at which this increases with the increase of dilution. Thus in Plate I., Figs. 1 and 2, the two groups lie wide apart, and while the first (HCl, etc.), show slight curvature, those of the second show rapid change in curvature in the region of great dilution.

(4) It appears from the regular course of the results, especially when exhibited in the various curves, that there is nowhere in the region studied any sudden change in the nature of the solution, so far, at least, as its freezing-point is concerned. The irregularities which appear (KCl, $KNO_3$) indicate that the experimental error at these points is very large, at least 0°.0006 C., and though this is much larger than seems to be admissible from the other results, still I think the course of the curves in the other regions indicates that the irregularities in extreme dilution are due to errors.

[1] Zeit. Phys. Chem., Bd. II., p. 496. [2] *Ibid.*, Bd. XII., p. 623. [3] *Ibid.*, p. 628.

(5) In view of the wide difference in the freezing-points of the more concentrated solutions belonging to the same group, it is a remarkable fact that the curves representing their molecular depressions converge rapidly as the dilution increases, and in such a manner as to suggest that *in extreme dilution they have perhaps sensibly the same freezing-points.* This convergence is the more striking when it is observed how widely the two extremes in the second group, $MgCl_2$ and $Na_2SO_4$, differ in their freezing-points at the concentration $m=0.30$. (See Plate I.) Here the freezing-points of the two solutions differ by 0°.395 C., while at $m=0.01$ they differ by only 0°.0004. So also in the first group, the two extremes, HCl and KCl, differ at $m=0.30$ by 0°.07 C., while at $m=0.01$ the difference is inappreciable.

The exceptions to be noted are $NH_4Cl$ and $KNO_3$ in the first group, and $BaCl_2$, $H_2SO_4$, and $MgSO_4$ in the second group. (For $MgSO_4$ see former paper.) The last two are vital exceptions. The others show such confusion in the curves in the region of great dilution as to indicate, as stated above, experimental errors.

It is to be observed that $H_3PO_4$ stands by itself, and in spite of the fact that it contains a trivalent radical, it depresses the freezing-point less than the group containing the univalent radical. I hope to be able to study other analogous compounds to compare their freezing-points with those of $H_3PO_4$.[1]

[1] In regard to the present values for phosphoric acid, it needs only to be remarked that the former series were known to have no significance, except so far as the regularity of the observed depressions might throw light upon the accuracy of the method.

It was distinctly stated that the "phosphoric acid" showed abnormal values, both in its specific gravity and electrical conductivity,* amounting in the latter to 7%. The particular specimen was the only phosphoric acid at hand, and since it had been known to be pure some years before, I used it for my work. Upon testing it, the fact of its great impurity was found, as stated in the note to which reference has been made. The present acid is from Trommsdorff. The normal solution was titrated by Mr. Hullet, and was then analyzed by him and found to contain 70.92 g. $P_2O_5$ per liter. This corresponds to a *gram-molecular* strength of 0.3329 instead of $\frac{1}{3}$, as required by the titration. The difference is altogether negligible. Its specific gravity is now in exact accord with that found by Kohlrausch, though the electrical conductivity is 209, instead of 200, as given by him.

* See Note, Physical Review, Vol. I., p. 282.

*Relation of Results to Dissociation Theory.*

The relation of the present results to the "Dissociation Theory" may be seen by comparing the observed depressions $\Delta$ in column (3) with those in column (6), which express the values of the depression computed on the basis of this theory.[1]

The theoretical values of the molecular depression are also found in column (5).

The theory assumes that the degree of dissociation in any given solution is represented by the ratio $\frac{\mu_x}{\mu_\infty}$, in which $\mu_x$ is the molecular conductivity of the solution for the given concentration $x$, expressed in gram-equivalent molecules per liter, and $\mu_\infty$ is the limiting value of this conductivity as $x$ approaches zero as its limit, or, as more generally expressed, the value of the molecular conductivity in infinite dilution. For $\mu_x$ the values as found by Kohlrausch are chosen, and for $\mu_\infty$, I have taken the most probable values as assigned by him.[2] Van't Hoff's constant is taken as he gives it, 1.89.

In the cases of $NH_4NO_3$ and $MgCl_2$, data for computing the theoretical values of $\Delta$ and $\frac{\Delta}{m}$ are not at hand. In case of $H_3PO_4$ no theoretical values are given, since at present there seems to be insufficient knowledge in regard to the *manner* of its dissociation.

It must be remembered that the concentration of the solution is represented by Kohlrausch by $\mu$, which expresses the concentration in gram-*equivalent* molecules, while in the present paper $m$ represents concentration in *gram-molecules*. Thus the solution, $BaCl_2$, $m=1$, is represented by Kohlrausch as $BaCl_2$, $\mu=2$, and the solution which would be represented by Kohlrausch as $H_3PO_4$, $\mu=1$, would be represented here by $H_3PO_4$, $m=\frac{1}{3}$.

The values in columns (5) and (6) which are inclosed in parentheses are found by graphic interpolations, and are subject to considerable error in the region of greatest concentration.

In addition, column (7) contains the difference between the

[1] See notes in former paper Physical Review, Vol. I., p. 286, (1), (2), and (3).

[2] Wiede. Ann., No. 26, pp. 198 and 204.

observed and computed values of the depression $\Delta$, and for the sake of readier comparison column (8) expresses this difference in *per cents* of the observed values.

*Remarks on the Bearing of the Results on the Dissociation Theory.*

It cannot be denied that in the cases of KCl and $K_2SO_4$ the agreement is practically complete. And in the cases of $NH_4Cl$, HCl, $BaCl_2$, $Na_2SO_4$, $KNO_3$, $NaNO_3$, the agreement is still surprising, and could hardly be set aside as "accidental." The differences, however, in these latter cases at least cannot be explained on the ground of some constant experimental error, since this would require that all the observed values should be uniformly either "too high" or "too low." While in general the present results are found to be lower than the theoretical values, it must be observed that in the cases of $BaCl_2$ and $Na_2SO_4$ they are *higher.*

It is further a matter of surprise that the two cases which show marked differences between observed and theoretical values are $K_2CO_3$ and $Na_2CO_3$, exactly the two where the uncertainty in regard to the value of $\mu_\infty$ makes any computation of the theoretical values little better than a guess. No doubt the most probable value of $\mu_\infty$, taking into account the general course of all the other curves in Kohlrausch's graphic representation of his results,[1] is that selected by him, 140 in case of $K_2CO_3$, and 122 in case of $Na_2CO_3$. If one, however, chooses the highest *observed* value of $\mu$ for the limiting value $\mu_\infty$, *i.e.* 122 for $K_2CO_3$, and 104 for $Na_2CO_3$ (plainly an arbitrary choice so far as present knowledge goes), then the theoretical values of the depressions become almost identical with those observed for the dilute solutions of $K_2CO_3$, and even in the case of $Na_2CO_3$ the agreement is perhaps all that the advocates of the theory require. (See Tables, column (8), for the two sets of percentage difference for $K_2CO_3$ and $Na_2CO_3$.)

As has been before remarked, the course of the curves for the molecular depression of $BaCl_2$, $NH_4Cl$, and $KNO_3$ indicates that in the region of greatest dilution the values are apparently affected

[1] Wiede. Ann., 26, No. 10, Figs. 1 and 2

by exceptionally large experimental errors, and it now appears that these apparent errors occur at the points where the difference between observed and theoretical values are found to be the greatest.

In regard to the differences, in general it may be said that they amount to 2.5%, which represents, in the case of extreme dilution, a difference, say, of 0°.0015 C. As the concentration increases, the percentage difference generally increases, reaching 6 % in the case of $BaCl_2$ for $m=0.20$. In general, in the greater concentrations the percentage difference may be put down roughly as 3 %, where it represents an actual difference extending into the *hundredths* of a degree. These differences, both in the dilute and in the concentrated solutions, are many times greater than any experimental error which the method and its results would seem to make admissible.

Further, it must be said that the dissociation theory requires uniformly that the potassium salts should depress the freezing-point more than the corresponding sodium salts. This follows directly from the fact that the degree of dissociation is uniformly greater in the case of the potassium salts. The present results, however, show the reverse, except in the case of the carbonates.

In case of the nitrates, the confusion of the curves in extreme dilution makes any comparison of the depressions difficult.

The KCl depressions are less than the NaCl, but it is to be remembered that the NaCl series was the one series made at a room-temperature of 18° C., and I now know that trustworthy results are to be had only at temperatures not far from 0° C. I think it necessary to repeat the NaCl observations before any final comparison between the KCl and NaCl depressions should be made, though in regard to the observations at $m=0.40$ there is no doubt; the NaCl depresses the freezing-point much more than the KCl.

### *Accuracy of the Method.*

It will be remembered that in the former paper, the experimental data were presented from which the reader was able himself to estimate the method's accuracy. No attempt was made

to fix its numerical value. The same course will be followed here, and the greater amount of experimental material now at hand throws much light upon this important matter.

Now, as then, these two questions are fundamental: —

(1) How far can one rely upon the constancy of these fine mercury thermometers?

(2) What sort of agreement exists between the individual observations of a series whose *mean* value is taken as the required freezing-point?

The answer to the *second* question given in the former paper is entirely unaffected by the new material. Now, as then, a series of five entirely distinct observations show on the average a variation of 0°.001 C.

This variation may be attributed to three causes: first, assuming the temperature of the solution in each of the different observations to be the *same*, then the variation could be referred to the inconstancy of the thermometer itself; second, assuming that the thermometer actually records the temperature of its "bulb," then the variation could be referred to the failure of the method to bring the solution to its "freezing-point" in each of the separate determinations; third, the variations in the temperature of the mercury projecting into the air is able to account for the variation. *The variation cannot be referred to reading errors.* Reading errors play absolutely no part in the experimental errors of the present method. There is no doubt that a $\frac{1}{100}°$ thermometer may be *read* accurately to the 0°.00005 C. The question is, would these *readings* indicate anything in regard to the *temperature* of the solution.

Since the reading error in comparison with the errors referred to above is insignificant, I have directed my attention entirely to the elimination of the latter rather than to the entirely superficial refinement of reducing reading errors either by using larger powers in the reading microscope or finer graduation of the thermometer.

In regard to the *first* question stated above, the same method of answer will be observed as in the former paper.

For this purpose the following table is given of all the observed

zero-points of the thermometer during the three months of the observations.

TABLE III.

| 1 Date, 1895. | 2 Barometer. | 3 Room-temperature. | 4 Observed zero-point. | 5 Zero-point corrected to 0° C. and 760 mm. |
|---|---|---|---|---|
| | | ° | ° | ° |
| Jan. 2 | 762.0 | + 5.0 C. | 0.0416 | 0.0397 |
| 7 | 759.7 | 10.0 | 0.0435 | 0.0404 |
| 14 | 756.7 | 0.0 | 0.0407 | 0.0412 |
| 21 | 756.0 | 2.0 | 0.0416 | 0.0416 |
| 25 | 765.3 | 2.0 | 0.0413 | 0.0397 |
| 28 | 764.3 | 0.0 | 0.0404 | 0.0397 |
| 29 | 754.1 | 2.0 | 0.0393 | 0.0397 |
| 30 | 757.4 | 0.0-4.0 | 0.0391 | 0.0389 |
| Feb. 4 | 754.4 | 3.0 | 0.0402 | 0.0402 |
| 5 | 760.1 | 3.0 | 0.0402 | 0.0392 |
| 11 | 760.6 | 4.0 | 0.0407 | 0.0394 |
| 13 | 746.9 | 2.0 | 0.0402 | 0.0418 |
| 18 | 754.6 | 5.0 | 0.0420 | 0.0414 |
| 20 | 754.1 | 6.0 | 0.0422 | 0.0414 |
| 25 | 759.8 | 4.0 | 0.0420 | 0.0408 |
| 27 | 761.6 | 5.0 | 0.0426 | 0.0407 |
| Mar. 4 | 754.5 | 8.0 | 0.0439 | 0.0423 |
| 5 | 764.0 | 9.0 | 0.0457 | 0.0422 |
| 6 | 769.4 | 7.5 | 0.0455 | 0.0416 |
| 13 | 761.1 | 10.0 | 0.0460 | 0.0427 |
| 14 | 758.4 | 10.0 | 0.0450 | 0.0421 |
| 18 | 754.0 | 7.0 | 0.0432 | 0.0420 |
| 19 | 757.6 | 6.5 | 0.0420 | 0.0404 |
| 20 | 759.2 | 5.0 | 0.0416 | 0.0402 |
| 25 | 757.7 | 7.5 | 0.0437 | 0.0417 |

The table needs no explanation further than to say that the correction for pressure was determined in the Reichsanstalt, Berlin, and given in the certificate accompanying the thermometer as 0°.001 C. for a change of 6 mm. in barometric pressure. The correction for room-temperature is the usual one, in which it is assumed that the entire mercury column in the air is at room-temperature. The apparent coefficient of expansion for mercury in glass is taken as 0.000156.

The results are graphically represented in Plate II., Fig. 6, where the dotted zigzag line shows the observed zero-point and

the full zigzag line represents the corrected zero. The scale is 5 mm. to the $\frac{1}{1000}°$ C. It thus has the same sensibility as the curves of molecular depression possess in the region of extreme dilution. Since the length of a $\frac{1}{100}°$ division in the thermometer is 0.4 mm., the actual observed variations in the thermometer are magnified 125-fold in the "curve."

It is to be observed: —

(1) The zero of the instrument has risen during the period of its rest at ordinary temperatures (March, 1893–January, 1895) from 0°.029 to 0°.040, or roughly at the rate of 0.0005 C. per month. This would produce a rise of 0°.0015 C. during the period of the observations. In Fig. 6 the straight line represents such a uniform rise of 0°.0015 C. during the three months. The actual observed rise is 0°.0020 C., an agreement which most likely is altogether accidental, since, of course, the assumption of a uniform rise of the zero-point of a thermometer is not warranted, even though the instrument, as in this case, has been long "seasoned."

(2) It is no less remarkable that the zigzag course of the zero-point seems to be governed by two *laws;* first, when the thermometer rested for more than a single night the zero remained either constant, as during the period Jan. 25–28 and Feb. 5–11, or else rapidly rose, as during the periods Feb. 11–13, Feb. 27–Mar. 4, etc. The only exception is the period Jan. 21–25. Second, when the thermometer was used two days in succession the zero-point is found on the second day to be sharply depressed, thus Jan. 29–30, Feb. 4–5, etc. The only exception here is Mar. 4–5. Could it be that the long-continued jarring of the thermometer during a day's observations should *depress* its zero! and that it recovered itself during the longer intervals of rest! The results seem to indicate these conclusions. These two singular regularities which appear to characterize the zigzag course of the observed zero-point were not known to me until the results were plotted in Fig. 6, long after the work was done, and I have thus had no opportunity to test the foregoing conclusions.

This series of freezing-points shows us that the *observed* zero-point of the thermometer was by no means constant.

This must be carefully considered.

On the one hand we may assume that the lack of constancy is only *apparent*, and to be explained on the ground of experimental errors. Accordingly the zero for Jan. 21 would be assumed to be 0°.001 C. too high, and on Jan. 25 as much too low. Similarly at Jan. 30 and Feb. 4, and at Feb. 11 and 13, in which latter case opposite errors, amounting to 0°.0015 C., would be assumed. (See Fig. 6.) These errors would then appear as errors in the depressions which were measured from the faulty zero-points, and since they would have to be assumed to be very great, we should find great irregularities in the curves of molecular depressions. For the most part such irregularities are entirely wanting. A closer analysis of the results in this respect is not without value. To this end let us examine the individual depressions measured on the days when these assumed erroneous zero-points were taken.

Jan. 21. — Zero-point apparently too high.

The depressions measured on that day were

$BaCl_2$, $m = 0.01, 0.02, 0.05, 0.10, 0.20$.

Our assumption that the zero-point was too high would make the observed depressions too great in the dilute solutions. The curve seems to indicate that they are too small.

Jan. 25. — Zero-point apparently too low.

$NH_4Cl$, $m = 0.01$, was repeated and a result was obtained which was 0°.0005 C. *higher* than the mean value of the table. Thus here the assumption that the zero-point was too low on this day does not accord with the observed depression.

Jan. 30. — Zero-point apparently two low.

The solutions observed were

$KNO_3$, $m = 0.01, 0.02, 0.05, 0.10$, and $0.20$.

In this case the assumption that the zero-point was erroneous agrees with the apparent error in the curve.

Feb. 4. — Zero-point apparently too high.

The entire series, $Na_2CO_3$, was observed.

The curve is entirely regular. This, however, would not decide whether the zero-point was too high or too low, since a perfectly regular curve would result even with a faulty zero-point, providing all the freezing-points of the solutions were themselves *without* error, or affected only by constant errors.

Feb. 11. — Zero-point apparently too low.

$MgCl_2$, $m = 0.15$ and 0.25, observed.

The curve at these points is slightly depressed and a possible error may be assumed which would be in accord with the assumption that the observed zero-point was too *low*.

Feb. 13. — Zero-point apparently too high.

$MgCl_2$, $m = 0.30$, was observed. The curve at this point is not "sensitive" enough to allow any judgment of possible error.

Feb. 27. — Zero-point apparently too low.

KCl, $m = 0.035$ and $NH_4Cl$, $m = 0.035$, observed.

The irregularity in the KCl curve would suggest, however, an opposite error in the zero-point.

Mar. 4. — Zero-point apparently too high.

$K_2CO_3$ complete series.

Here, as in the case of $Na_2CO_3$, the curve presents no irregularities. (See remark under Feb. 4.)

Mar. 6. — Zero-point apparently too low.

The rejected series, KHO and NaHO, $m = 0.01$ and 0.02, were made. The curves were without irregularities, and were rejected, as has been stated already, because their specific gravity and electrical conductivity were found to be abnormal.

Mar. 13. — Zero-point apparently too high.

$NaNO_3$ and $NH_4NO_3$, $m = 0.01$, 0.02, and 0.03, were observed.

The curves suggest no errors in this region.

Mar. 20. — Zero-point apparently too low.

$KNO_3$, $m = 0.025$, $NaNO_3$, $m = 0.20$, and $NH_4NO_3$, $m = 0.20$, were observed.

The observed points in the three curves are perfectly regular and point to no error.

Mar. 25. — Zero-point apparently too high.

$H_3PO_4$ entire series observed.

The curve is perfectly regular and suggests no error. (See remark under Feb. 4.)

It thus appears that the assumption that the zero-points were erroneously observed on the days when the marked zigzags occur in the "curve" of zero-points is insufficient to explain the observed changes in the zero-point of the thermometer, since, if this were the case, the corresponding errors would, in general, appear in the measured depressions. We are thus obliged to admit that

the thermometer itself is subject to serious changes, which, however, do not seem to be *sudden* as was concluded from the former study of this point, but still of such a nature as to render serious errors possible.

While close comparison with the results of other methods, some of which are more recent, seems to indicate that in the present method the errors are clearly reduced to the limits attained by other observers, still I think any rational interpretation of the present results requires the admission of experimental errors sometimes as high as 0°.001 C. It is for this reason that I have never thought it profitable to employ the method beyond the dilution $m=0.01$, since in this region an error of 0°.0001 C. is fatal.

### *Remark on Bias.*

It seems important to add that no effort has been spared to eliminate this source of error. While the method seems to make it impossible that the observer's bias should have any influence on the results, still the further precaution has been taken in every case to *complete* the five usual observations in a series before reducing the results to co-ordinate paper. Further, in no case was any comparison with the results of other observers made until after the entire work of observation was complete; and finally in no instance were the so-called theoretical values calculated until months after the work was finished, when the work was in preparation for publication.

In conclusion I may add it is hoped to extend the observations as soon as the temperature conditions will permit, so as to include $HNO_3$, KHO, NaHO, and $NH_4HO$, a series of phosphates, and various organic compounds.

PRINCETON, N. J., Aug. 16, 1895.

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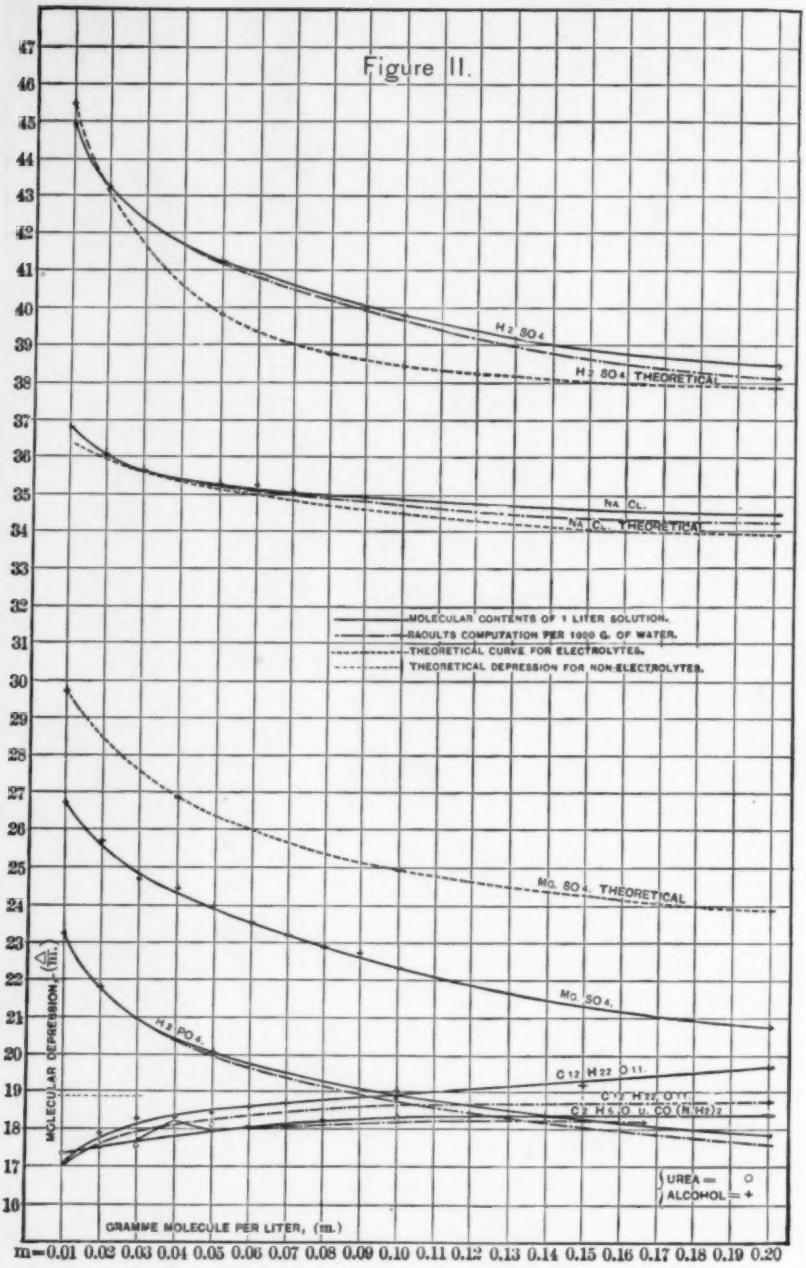


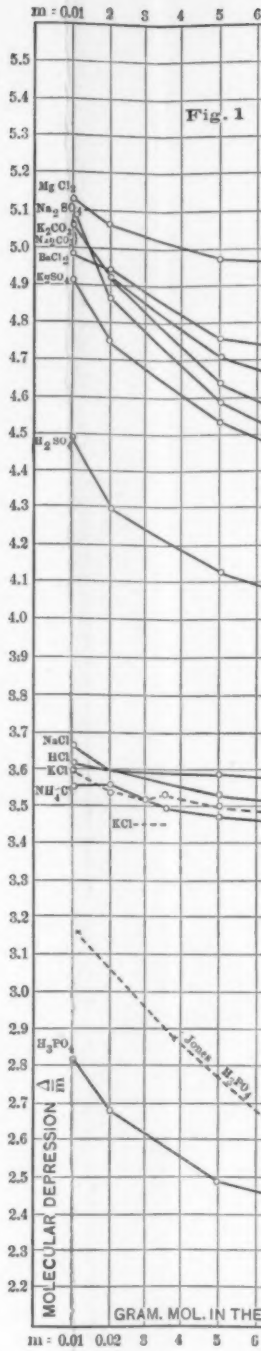


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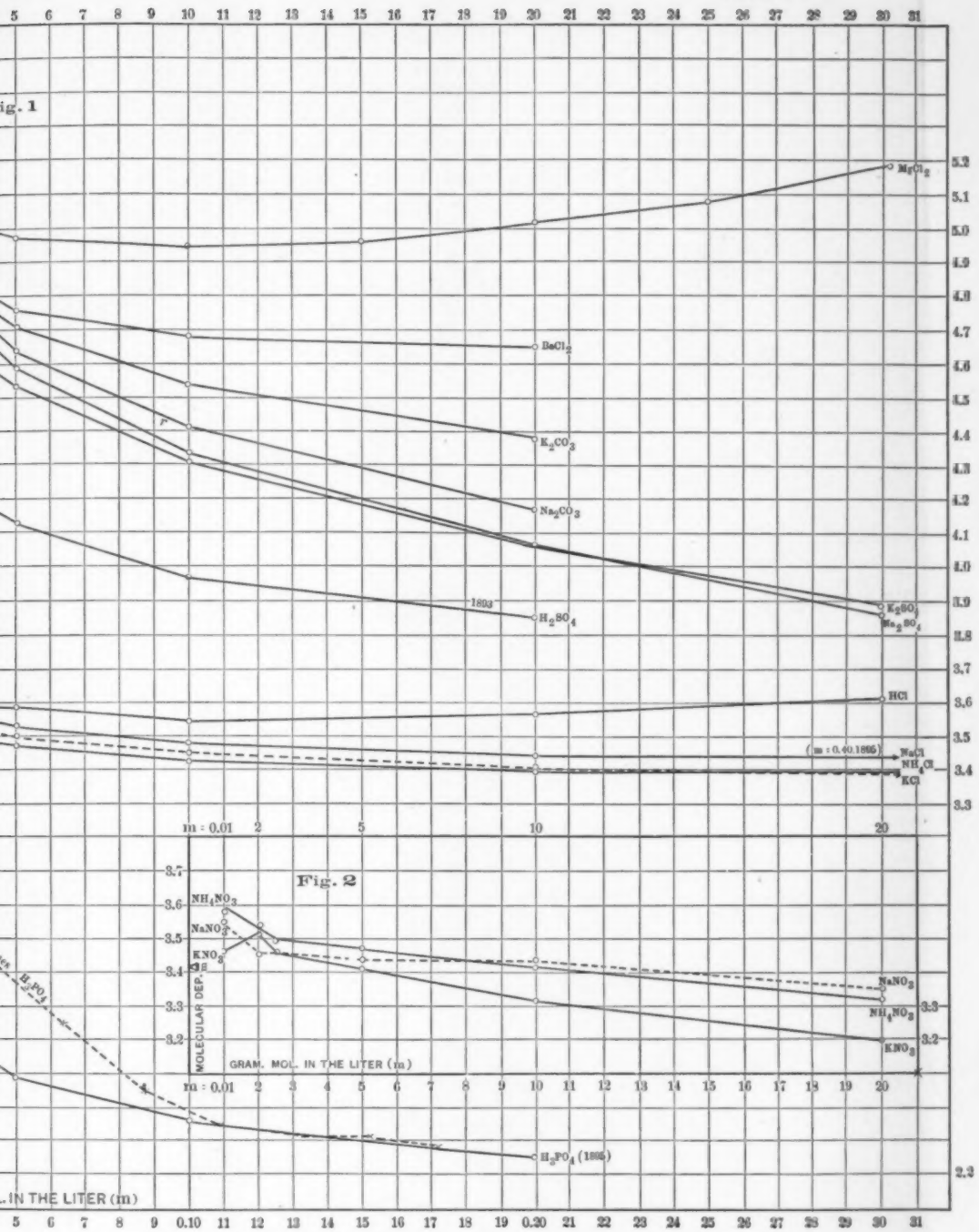


Fig. 1
$MgCl_2$
$BaCl_2$
$K_2CO_3$
$Na_2CO_3$
1893
$H_2SO_4$
$K_2SO_4$
$Na_2SO_4$
HCl
(m = 0.40 1895)
NaCl
$NH_4Cl$
KCl
$H_2PO_4$
$H_2PO_4$ (1895)
IN THE LITER (m)


Fig. 2
$NH_4NO_3$
$NaNO_3$
$KNO_3$
$NaNO_2$
$NH_4NO_2$
$KNO_3$
MOLECULAR DEPRESSION
GRAM. MOL. IN THE LITER (m)

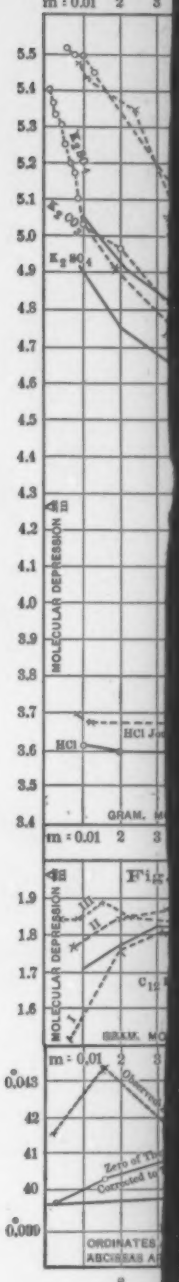
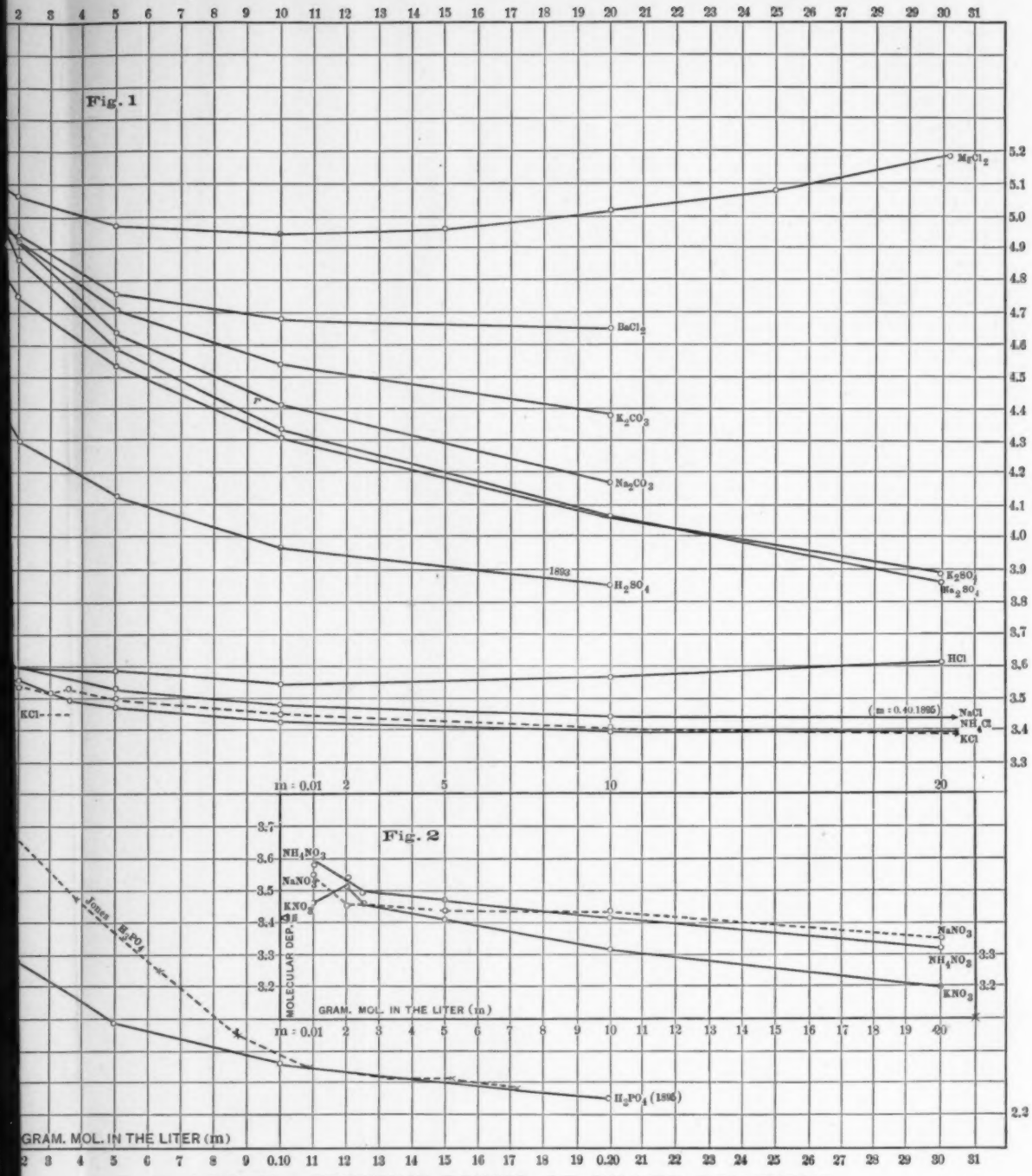
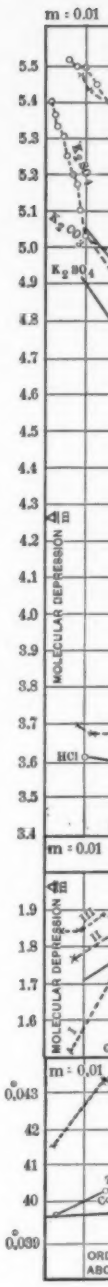

MOLECULAR DEPRESSION
HCl
GRAM.

PLATE I.




E. H. LOOMIS: FREEZING-POINTS OF DILUTE SOLUTIONS.

PLATE II.

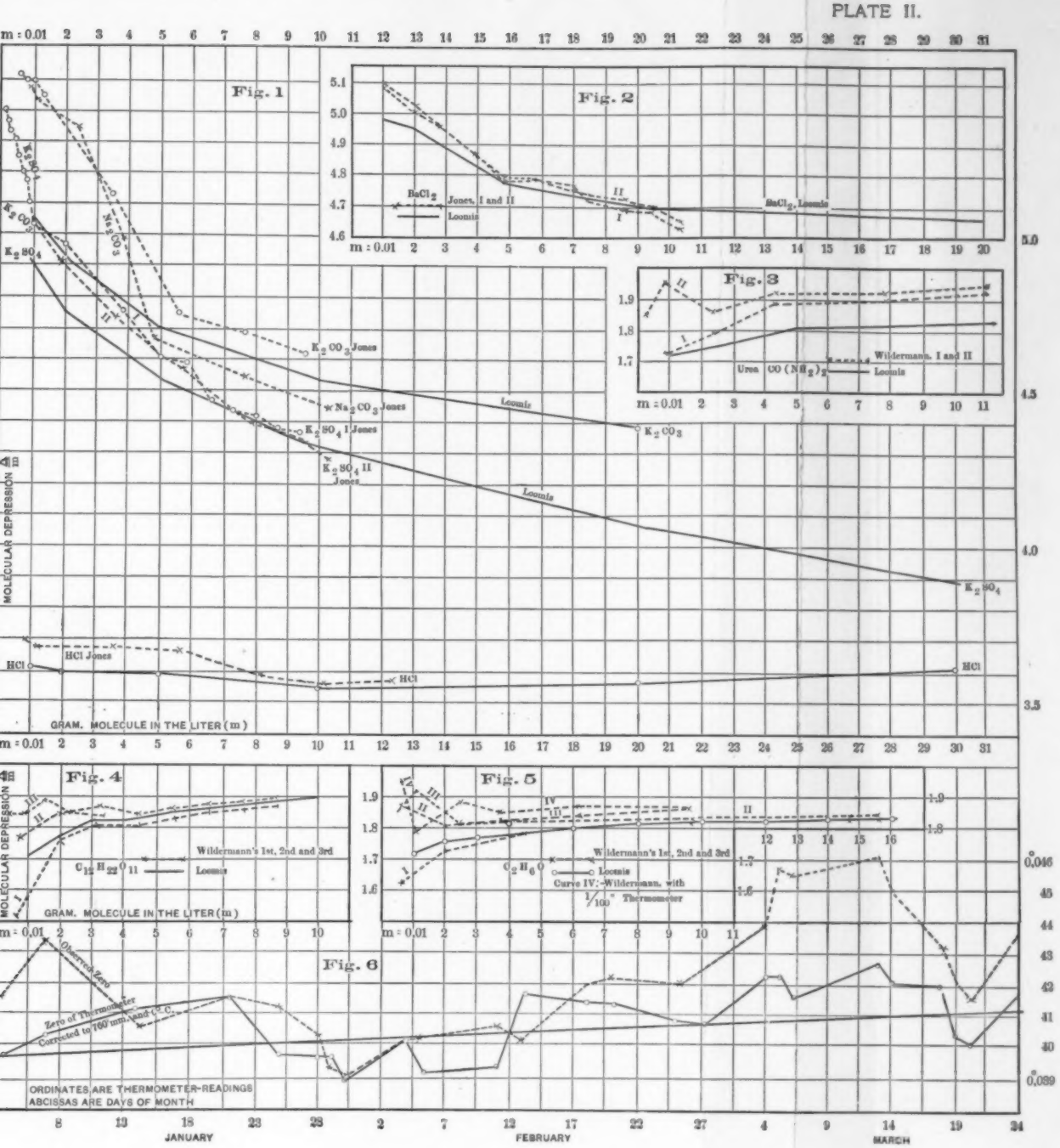


Fig. 1
Fig. 2
Fig. 3
Fig. 4
Fig. 5
Fig. 6
MOLECULAR DEPRESSION
GRAM. MOLECULE IN THE LITER (m)
m = 0.01
$K_2SO_4$
$K_2CO_3$
$Na_2CO_3$
HCl
$K_2CO_3$ Jones
$Na_2CO_3$ Jones
$K_2SO_4$ I Jones
$K_2SO_4$ II Jones
HCl Jones
Loomis
$BaCl_2$
$BaCl_2$, Jones, I and II
$BaCl_2$, Loomis
Urea $CO(NH_2)_2$
Wildermann, I and II
$C_{12}H_{22}O_{11}$
Wildermann's 1st, 2nd and 3rd
$C_2H_6O$
Curve IV:-Wildermann. with 1/100° Thermometer
Observed Zero
Zero of Thermometer Corrected to 760 mm. and 0° C.
ORDINATES ARE THERMOMETER-READINGS
ABCISSAS ARE DAYS OF MONTH
JANUARY
FEBRUARY
MARCH

# MINOR CONTRIBUTIONS.

## Some Questions in Regard to the Author's Method of measuring Freezing-Points of Dilute Solutions.

By E. H. Loomis.

THE observations which the present writer submitted on the freezing-points of some dilute organic solutions were so radically different from all the results of the previous observers that various questions have arisen in regard to them.

1. Mr. Jones[1] has kindly suggested that the wide divergence between his results and mine may be explained, perhaps, by my having used impure materials, particularly in the case of sugar and phosphoric acid. The latter has been discussed sufficiently in the preceding paper, p. 283, note. In regard to sugar it is to be said that only *well formed, transparent* crystals of "sugar candy" were used. These were carefully selected, and were freed from dust with a fine brush. They were then pulverized and dried over sulphuric acid. The properly weighed amount was then dissolved in *cold* water (4° C.), and the freezing-points were determined as soon thereafter as possible. I think such material may be safely regarded as well within the limits of purity required by present methods in freezing-point determinations.

In general it is to be remarked that I have uniformly given chief attention to the reduction of experimental errors in the physical part of the work rather than the chemical, since it seems the former errors have been and still remain the great difficulty, in comparison with which the question of absolute chemical purity of the materials is hardly to be considered.

2. *Is it not possible that some source of experimental error peculiar to the method which I employ may account for the fact that the results are uniformly lower than those of all previous observers.*

In regard to this it is to be said that the continued practice of the method has developed no knowledge of any such experimental error. In this connection it is an interesting fact that all the more recent determinations *agree* in a marked lowering of the old values for these organic compounds, while some of them, more noticeably those of Nernst and Abegg[2]

[1] Wiede. Ann. 58, 1894, p. 395. [2] Zeit. Phys. Chem., 1894, 4, p. 681.

and Wildermann,[1] are almost identical with mine in the region of middle concentration. This agreement becomes more striking from a glance at the following table, which I here reproduce from the former paper.[2] It contains the freezing-points of a $\frac{1}{10}$ normal sugar solution as found by the various observers named, together with the year of publication and the estimated error of the observers.

To this table I now add my own value and the values of the more recent observers.

| Observer. | Year of Publication. | Freezing-point. | Estimated error. |
|---|---|---|---|
| Raoult I. | 1886 | 0°.24 | 0°.01–2 |
| Arrhenius I. | 1888 | 0°.210 | 0°.0–05 |
| Traube | 1891 | 0°.235 | 0°.005 |
| Eykmann | 1891 | 0°.216 | — |
| Arrhenius II. | 1891 | 0°.204 | — |
| Tammann | 1891 | 0°.206 | — |
| Pickering | 1891 | 0°.202 | 0°.0005 |
| Raoult II. | 1892 | 0°.205 | 0°.002 |
| Loomis | 1893 | 0°.190 | — |
| Jones | 1893 | [3] 0°.197 | 0°.0001–2 |
| Nernst and Abegg | 1894 | [4] 0°.187 | — |
| Wildermann | 1894 | [5] 0°.190 | 0°.0001–2 |

3. It has been suggested by Mr. Wildermann in regard to the three organic compounds examined by me *that the observed increase in the molecular depression with the increase of concentration may be due to some experimental error which he thinks may have rendered the observed zero point too low.* The results hardly admit of this assumption, since the assumption would be justified only by a succession of constant *differences* between the freezing-points of the successive solutions, $m = 0.01$, $m = 0.02$, $m = 0.03$, etc., to $m = 0.20$. These *differences*, however, show an unmistakable increase, which in the case of sugar is from **0°.0184** to **0.0206**. That is, the addition of each $\frac{1}{100}$ gram-molecule to the solution lowers the freezing-point by an ever-increasing amount. We conclude then that the observed increase of molecular depression cannot be due to any error

[1] Zeit. Phys. Chem., 1894, 3, p. 337. [2] Phys. Review, Vol. I., 1893, p. 200.

[3] Graphic interpolation. Mean of two series which differ in this region about 0°.002.

[4] Extrapolation. Mean of three series which differ so widely in their essential nature that the extrapolation is very uncertain.

[5] Very slight extrapolation.

in the determination of the zero point of the thermometer. The same remarks apply to the results for alcohol and urea.

Further, such an error would necessarily be a *constant* error, as these three compounds were studied in precisely the same manner as all the other compounds, now numbering some twenty. That these other results seem to be free from such a constant error makes the given assumption at least improbable. That the supposed error could have been an *accidental* error peculiar to two or three determinations of the zero point from which the depressions were obtained, is impossible, since these particular depressions for sugar and alcohol were measured from no less than *fourteen* separately determined zero points, each of which was the mean of 7–9 entirely independent observations.

It seems well to compare my results in this particular with those of other observers. Among the previous observers, Arrhenius and Tammann each had observed this increase of molecular depression with increasing concentration. Of the more recent observers all except Mr. Jones find the same increase which I have observed. Thus the results of Nernst and Abegg[1] for sugar, although their three separate series of observations differ very widely among themselves, — one series showing an *increase* of molecular depression with the increase of concentration, a second, a decrease, and the third presenting such irregularity that no conclusion may be drawn from it in this regard, — still the *mean* values of the three series show a pronounced *increase*. Jones' results show the same increase from the point $m = 0.10$; Raoult's results from the point $m = 0.16$, while those of Wildermann show this increase throughout the *entire* region. See Fig. 4, Plate II., where Wildermann's results for sugar are represented by the dotted lines. Curve I. was made with an "ice cap" about the bulb of his thermometer, II. without this "ice cap," while III. was made under still "more favorable conditions."[2] Mr. Wildermann regards II. as correct to within $0°.0001$–$2$ C. The three facts, then, which appear in this remarkable series must be looked upon as final.

1. There is a marked *increase* in the molecular depression from the value 1.76 in the most dilute solutions, to 1.89 in the most concentrated.

2. The molecular depression reaches the value 1.89 *only* in the most concentrated solutions, where Mr. Wildermann tells us, later, the value can have no significance.

3. The series shows no tendency to become constant at this highest observed value, since a glance at the curve in Fig. 4 makes it plain that the results merely cross the horizontal line of constant molecular depression, 1.89.

[1] Zeit. Phys. Chem. 189, p. 681.

[2] Phil. Mag. 1895, No. 242, p. 126.

Having reached this value 1.89, Mr. Wildermann stopped his investigation.

Mr. Wildermann *says* of this interesting series, "der *constante* Werth (1.89) kommt sehr gut zum Vorschein."

As Mr. Wildermann explains a similar increase of the molecular depression in series I. as due to the "ice cap" about the thermometer bulb, it would be desirable to know on what grounds he sets it aside in Series II., where no "ice cap" was at hand.

Although this Series II. is regarded by Mr. Wildermann as correct to within $0°.0001-2$, still it does not seem to have been so conclusive to Mr. Wildermann as his discussion of it would seem to indicate, since he repeated the work "under more favorable conditions."[1] As a result we have Series III. This new series differs irregularly from Series II. by about $0°.001$, — or about five-fold the possible error of the former series. If this Series III. is now to be taken as having reached the utmost limits of experimental accuracy, we must, I suppose, conclude that Mr. Wildermann underestimated the experimental error of his former work.

The unprecedented accuracy of this final series makes it worthy of attention (see Fig. 4, Curve III.).

1. It shows a variation from 1.84 to 1.89.

2. The value 1.89 is reached very abruptly by one only of the five observations. This value is preceded by two observations whose values are 1.84, and followed by two whose mean value is also about 1.84.

Still Mr. Wildermann *says* of this series of observations: "Thus I have shown that the constant (1.87–9) holds good in dilute solutions."[1]

This divergence between Mr. Wildermann's results and his interpretation of them should be kept constantly in mind in studying his work.

Thus in the case of alcohol (see Fig. 5, Plate II.) his results obtained "without ice caps" (Curve II.) show a steady *increase* of molecular depression from 1.81 to 1.85. The only exception is at $m = 0.006527$. Now Mr. Wildermann says[2] of these results: "*We obtain the constant value 1.84 in all concentrations.*"

The third series, "repeated under more favorable conditions," shows even more strikingly the same unmistakable increase of the molecular depression with the concentration. I do not think it profitable to extend this examination to the remaining case of urea where the same facts appear.

It may be well here to call attention to the remarkable agreement between Mr. Wildermann's results, obtained with "ice caps," and my own results for sugar and alcohol. This agreement in the case of alcohol (see Fig. 5, Plate II., Curve I.) is so close that the two series must be looked upon as identical except in the small region of greatest dilution. He explains

[1] Phil. Mag. No. 242, 1895, p. 126. [2] Zeit. Phys. Chem. No. 3, 1894, p. 342.

this agreement by saying that there was undoubtedly a similar "ice cap" about the bulb of my thermometer. If Mr. Wildermann will take the trouble to refer to my former publication, he will find that the formation of these ice layers was carefully discussed there, and will learn that one reason for confining the "overcooling" to the narrow limits, 0°.15 to 0°.25, was to make the building of these troublesome ice layers impossible. In fact, no *trace* of ice ever forms on either the bulb of the thermometer or wall of the freezing vessel.

This remarkable agreement is the more difficult to explain since Mr. Wildermann regards my results as "merely qualitative," and further says the concentrations of the various solutions were incorrectly determined.

4. *May not some such constant error as that discussed in* (3) *account for the fact that in the three non-electrolytes examined by me the "curves" of molecular depression, which differ so little from straight lines in the great part of their course, should all alike show a downward curvature in the region of extreme dilution?*

The results, I think, do not permit a final answer to this question. To render the "curve" a straight line throughout its entire course would require the admission of experimental errors by no means large, and it is perhaps well to regard this matter as still in doubt.

That such an error is not altogether improbable appears from the fact that in the case of those *electrolytes* which seem to be affected with errors in the region of extreme dilution a similar downward tendency of the curves appears ($BaCl_2$, HCl, $NH_4Cl$).

*The fact that Wildermann's results show this same peculiarity* should not be regarded in the light of a confirmation of my results.

5. A most important question still remains: *What are the respective advantages to be had by using a thermometer graduated in* $\frac{1}{1000}°$ *and one graduated in* $\frac{1}{100}°$?

I am able to discuss this question only on the basis of my own work with a $\frac{1}{100}°$ thermometer and the published results of other workers who have employed the $\frac{1}{1000}°$ instruments.

First, it must be emphasized that the $\frac{1}{100}°$ thermometers are easily read to the ten-thousandth of a degree with a possible reading error of half that amount. The sufficient proof of this is the fact that I have frequently interrupted a series of observations to allow some student who might happen to be present to make the reading for me. In *no case* have such readings differed from my own by more than $\frac{1}{10000}°$. This is not at all surprising since it is to be remembered that the micrometer scale in the microscope enables the observer to read the thousandths directly, and the *ten-thousandths* are as accurately estimated as the tenths of millimeters on an ordinary millimeter scale.

How, then, is the fact to be explained that a series of five independent determinations of a given freezing-point vary on the average about 0°.001? First, it must be due to the *inconstancy* of the thermometer itself, or second, to the failure of the method to bring the solution to its actual freezing-point by amounts within these limits. The first cause of variation has been discussed already.[1] While it undoubtedly plays some small part in this respect, still, I think it may be easily shown that the second cause is the all-important one, and represents the *fundamental difficulty* in all freezing-point determinations.

Thus, to cite the results of Mr. Jones,[2] it appears that the great accuracy with which he could *read* his $\frac{1}{1000}°$ thermometer, together with a few preliminary observations lead him to fix his *experimental* error at 0°.0001–2. Certainly the *reading* error is even less than that. The fact, however, appears throughout Mr. Jones' *results* that his method failed to bring the solutions to their freezing-points with this estimated accuracy, since in *every* instance where Mr. Jones furnishes us with two series of observations, the corresponding observations on the same solution frequently differ by $\frac{1}{1000}°$ and not rarely by two or three times this large amount. These surprising differences appear quite generally throughout his two $K_2SO_4$ series and $BaCl_2$ series. See Plate II., Fig. 1.

It would seem that a method which thus fails in the fundamental matter of bringing a solution to its freezing-point to within 0°.001–3 has little to gain by the use of a thermometer which may be read to 0.0001° C. That Mr. Jones seems to have become himself aware of this failure of his method to bring the solution to its freezing-point with any great degree of accuracy appears certain, since he explicitly refers to the *regularity* in the decrease of molecular depression shown by his HCl results.[3] See Plate II., Fig. 1, for the graphic reproduction of his results. That such a "curve" is regarded by Mr. Jones as *regular* indicates his belief that the method easily permits experimental errors amounting to several thousandths of a degree.

But we are not left to infer this knowledge on the part of Mr. Jones, since he says[4] of his results for $Na_2CO_3$: "Their *apparent irregularity* is due without doubt to a slight experimental error." See the graphic representation of his $Na_2CO_3$ results in Fig. 1, Plate II. It here appears that the "*apparent* irregularity" amounts to only a little less than a *hundredth* of a degree. That Mr. Jones should refer to this as a slight error shows how clearly he understood the complete failure of his method in the particular under discussion.

What is true of his $Na_2CO_3$ series appears also in all his later results,

[1] p. 287–91.
[2] Zeit. Phys. Chem., 1893–1894.
[3] *Ibid.*, 1893, xii., p. 628.
[4] *Ibid.*, p. 638.

*noticeably* in $H_2SO_4$, sugar, $BaCl_2$, $K_2CO_3$, etc. The curves for the two latter are given in Fig. 1 and Fig. 2, Plate II.

It is hard to see what particular advantage resulted from the use of a $\frac{1}{1000}°$ thermometer, or on what grounds Mr. Jones justifies his attempts to measure the molecular depressions of solutions in the extreme dilution, $\frac{1}{100}$ to $\frac{1}{1000}$ normal, where an experimental error of 0°.0001–2 is absolutely *fatal*.

The only other observer who has made use of a $\frac{1}{1000}°$ thermometer, so far as is known to me, is Mr. Wildermann in the application of a method devised by Mr. Lewis. That this method likewise fails in this fundamental matter of bringing the solutions to their actual freezing-points appears from a similar examination of the two series of results which he has furnished for both sugar and alcohol.

Series II. in each case is affected according to Mr. Wildermann with a possible error 1–3 ten-thousandths of a degree, and Series III. is regarded by him as made under "more favorable circumstances."

Among the differences which these two series for sugar present may be mentioned the following:

| | |
|---|---|
| At $m = 0.01$, | 0°.0008 |
| $m = 0.02$ | 0°.0004 |
| $m = 0.03$ | 0°.0006 |

while in the case of the alcohol series we meet the following:

| | |
|---|---|
| At $m = 0.01$, | 0°.0004 |
| $m = 0.02$ | 0°.0008 |
| $m = 0.05$ | 0°.0010 |
| $m = 0.09$ | 0°.0027[1] |

Unfortunately he does not publish a "repeated" series for urea, though we are left to infer that he made such a series, since he writes: "This year I repeated the investigations of cane sugar, alcohol, *etc.*"[2]

However, we are able to conclude from the data already at hand that his estimated experimental error, 0°.0001–2, is in fact about fivefold too small to explain his results.

I know of no way to explain these great differences except by supposing that the method failed to bring the various solutions to their real freezing-points by 1–2 thousandths of a degree. The great irregularity of his results would be explained by Mr. Wildermann, I suppose, in the same way. And yet Mr. Wildermann *reads* his thermometer to the ten-thousandth of a

[1] In order to obtain the actual difference of the two observed freezing-points one has to multiply the difference as given in the curves by the corresponding abscissa, or value of $m$.

[2] Phil. Mag., 1895, 242, p. 126.

degree, and to avoid *reading errors* makes from 5 to 10 observations of his thermometer. This is the more surprising when it is remembered that it is now quite generally understood that the mercury in one of these fine thermometers, when once it comes to rest in the capillary, remains *fixed* so long as the bulb experiences only slight changes of temperature (such as thousandths of a degree) and the thermometer is not vigorously *jarred*. Still Mr. Wildermann assumes that having brought his thermometer to a constant *reading* he has likewise brought his solution to a constant *temperature*.

How, then, does Mr. Wildermann account for the fact that his $\frac{1}{100}°$ thermometer placed side by side with his $\frac{1}{1000}°$ instrument shows variations of some thousandths (1–3)? He tells us that these are reading errors! Is it not perhaps possible that these variations may not be wholly due to carelessness in reading the instrument, but may arise from actual changes of the mercury! The $\frac{1}{100}°$ thermometer with its small bulb is perhaps able to thus indicate the temperature-changes in his solutions which would be wholly lost to his $\frac{1}{1000}°$ instrument with about *300 grams* of mercury in its bulb.

I think a careful analysis of the results obtained with a $\frac{1}{1000}°$ thermometer obliges one to conclude that its use as yet has added nothing to the accuracy of the various methods, and indicates that further accuracy is to be sought in the direction of greater control of the temperature of the solution itself.

In conclusion it may be well to point out a few matters which long practice seems to make worthy of attention.

1. It cannot be emphasized too strongly that the reading of the thermometer, whatever the method, should *never* be made until all manipulation of the solution is done with.

2. The experimental error of a given method may be safely estimated by making a series of entirely independent determinations of the freezing-point of *water*. These should be made on a day when the barometer is fairly constant, and special attention should be given to the matter mentioned in (1).

3. It seems to be important to preserve a record of all the observed zero points of the thermometer, together with the dates of observations. Thus the very great variation of 0°.008[1] in the apparent zero of Wildermann's $\frac{1}{1000}°$ thermometer, during the short period of his observations would perhaps lead to some valuable conclusions if systematically studied.

[1] The maximum is found on p. 339 (Zeit. Phys. Chem. 1894, III.), where the third observed zero point is 0.4873, which becomes, when reduced to 760 mm, 0.4884. The minimum is found on p. 362, when the observed zero is 0.4781, or reduced to 760 mm., 0.4804.

It remains to be added that there seems to be little profit in correcting the misstatements of Mr. Wildermann in regard to the work of the present writer.

PRINCETON, N. J., Aug. 15, 1895.

## A COMPARISON OF TWO CONCAVE ROWLAND GRATINGS.

BY ALICE H. BRUÈRE.

TO any one who has worked with the spectra produced by diffraction gratings, the irregularities which occur in them are only too well known. Even when the grating has been constructed with the utmost care in every detail of the work, as is the case with Professor Rowland's concave gratings, variations of intensity in the spectra of different orders, or in the different parts of a single spectrum, are peculiarities which it seems impossible to avoid, and the appearance of ghosts, or the lack of symmetry with respect to the focal distance of the various spectra, are matters of frequent observation.

Professor Rowland[1] notes and discusses many of these peculiarities in a paper published in 1893.

Kayser and Runge,[2] in their article upon the spectra of the elements, mention a sudden diminution of intensity for the shorter wave-lengths obtained from what, in other respects, was an exceedingly fine grating. This seemed extraordinary because the phenomenon was repeated at the same wave-length in the spectra of all orders, and could therefore not be attributed to the shape of the groove.

The asymmetry of gratings is discussed at length in an article upon his observations by Dr. Rydberg,[3] of the University of Lund, Sweden, in 1893.

F. Paschen,[4] in the same year, published some results of bolometric determinations of the spectra of glowing solids. Previous to the investigation, he believed that the conditions of his experiment were exceptional, because in obtaining the spectra by means of a concave grating he would avoid the difficulties which arise through the use of a rock-salt prism and lenses. The energy curves which he obtained were, however, irregular and discontinuous to such an extent, that it was evident the spectrum he was

[1] H. A. Rowland, Gratings in Theory and Practice, Astronomy and Astrophysics, 12, 1893. Phil. Mag. S. 5, 35.

[2] Kayser and Runge, Ueber die Spectren der Elemente; Abh. der Berl. Ak. der Wiss. 1888. Theil I.

[3] Dr. J. R. Rydberg, On a certain Asymmetry in Professor Rowland's Concave Gratings. Phil. Mag. S. 5, 35. Astron. and Astroph., May, 1893.

[4] F. Paschen, Bolom. Untersuchungen im Gitterspectrum. Wied. Ann. 48 [1893].

using was not fit for the purpose. Further investigation showed that all spectra thus obtained gave different curves for the same substance under exactly similar conditions of arrangement and temperature, and that all were equally irregular.

These and similar observations suggested a comparative study of two concave Rowland gratings belonging to the Physical Department of Cornell University, with a view to obtaining additional data upon the irregularities of gratings by a method not previously tried.

One grating is marked "14438 lines to the inch"; on the second, there is no statement with respect to the ruling, but all observations indicate that it is ruled with the same or nearly the same number of lines to the inch as the one marked. The length of radius marked upon each is six feet. Although not of the best Professor Rowland has ruled, the gratings are considered good.

The first experiment was a photometric comparison of the spectra obtained from the two gratings. For this purpose, the grating whose spectra appeared more nearly uniform was chosen as a standard. This one, for convenience, will be designated as grating "A," and the other as grating "B." The two gratings were mounted, one above the other, on a vertical support. The arrangement of the apparatus was similar to that of Professor Rowland in his spectroscopic work. By means of three screws back of each grating, they were adjusted until perpendicular, and then inclined toward each other enough to bring the two spectra on the screen sufficiently close for accurate observations.

The intensity of the spectrum obtained from a grating varies with the amount of light admitted to it. A comparison of the intensities of the spectra obtained from two gratings, receiving light from the same source, may therefore be made by comparing the widths of the slits through which light is admitted to them. All other conditions being the same, the ratio of these widths, when the spectra are of equal intensities, will be the inverse ratio of the intensities of the two spectra obtained with equal illumination on the gratings.

This was the method employed. The two gratings were illuminated by light from independent slits. A double slit was used, each part of which was operated by a micrometer screw. It was carefully mounted, with a screen horizontally before it. The latter was adjusted until the beams emerging from the two parts were completely separated. This occurred when the light on the gratings was divided by a sharp black line, the shadow of the screen, midway between them. When the two slits were adjusted so that the spectra obtained were of equal intensities, the measurement was taken in terms of the widths of the slits. For this reason these were carefully calibrated to thousandths millimeters.

The spectra were received upon a screen of oiled paper bent into an arc of the circle. The diameter of this circle was equal to the radius of the grating. Before the screen could be slid an opaque screen, in which a rectangular aperture about one centimeter in width had been cut. In this way the entire spectrum, except the part in which observations were to be made, could be cut off. During the observations upon one spectrum, the position of the translucent screen was fixed. For the best conditions, its position should have been at the focal distance of the spectra. It was impossible to place it so, however, for these distances differed for the two gratings by about six inches, and an intermediate position had therefore to be chosen. This introduced an error into the measurements, but as the entire distance was great as compared with the discrepancy, the error is small.

The light used was that from a zircon disk heated to incandescence by the oxyhydrogen flame. The time for one set of observations could not exceed one hour, for the sensitiveness of the eye diminished greatly if it was extended beyond this. For this length of time, the light from the zircon disk was found to be most brilliant and constant.

The screen was calibrated to wave-lengths by means of bright-line spectra. These were obtained by using an arc-lamp whose carbons were cored and filled with substances having distinct lines in well-known positions.

In the measurements, the slit which illuminated grating *A* was set at a fixed width. Comparisons were then made for a number of positions throughout the spectra of the first and second orders on both sides. The slit which illuminated grating *B* was adjusted until the spaces in the spectra were of equal intensities, and the width of the slit was then read in divisions of its micrometer screw-head. This could be reduced to thousandths millimeters from a calibration curve drawn for this purpose.

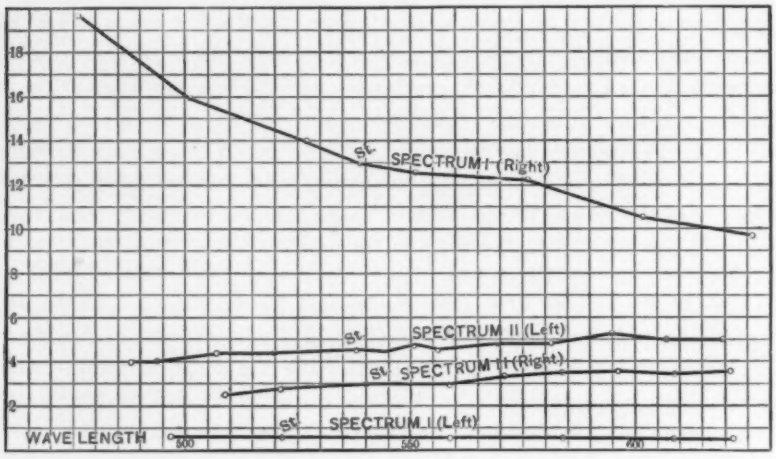
The intensity of a spectrum is dependent on three factors: the intensity of the light on the slit, the width of the slit, and the intensity due to the grating itself for unit width of slit and unit intensity on the slit. The product of the quantities expressing the values of these factors for grating *A* then expresses the true intensity for a given space in the spectrum obtained from this grating. Using corresponding quantities, the true intensity for the corresponding space in the spectrum from grating *B* may be expressed as a product. In the observations these intensities were made equal; we therefore have an equation between them.

Before and after each observation in a given part of the spectrum an observation was taken in that part of the spectrum to which the eye had been found to be most sensitive. This served as a check upon the ratio of the intensities of the light which fell upon the slits, since for any one position this was the only factor which could vary. A second equation was

obtained from the intensities at this position of reference. From the two equations, a value for the intensity factor due to grating *B* at a given position was obtained, involving only the ratios of the widths of the slits, and the ratio of the intensity factors due to the gratings at the position of reference. The former were directly obtained by the experiment; the latter, being always in the same part of the spectrum, was a constant.

Since only a ratio of the intensity due to grating *B* to that due to grating *A*, which was assumed as unity, was desired, this constant could be given any convenient value. With the product of the ratios of the widths of the slits by this value for ordinates, and wave-lengths for abscissæ, curves were drawn.

From the values for the ratios of the widths of the slits indicating the relation of the intensities of the two spectra, an average ratio for each of the




four pairs of spectra was obtained. On the left, that of spectrum I. to the standard was 0.5 : 5 ; that of spectrum II., 4.5 : 5. On the right, that of spectrum I. to the standard was 13 : 5 ; that of spectrum II., 3 : 5. If now the constant mentioned above be given the values, 0.5, 4.5, 13 and 3 in the respective spectra, and the product of the ratios of the widths of the slits by this quantity be platted as ordinates, and wave-lengths as abscissæ, curves are obtained showing the relation of the four spectra to each other. Each curve also indicates the variation throughout a single spectrum.

The adjoining curves have been obtained in this manner. The first spectrum to the left was an exceedingly weak one. The spectrum of the same order to the right, which was obtained by reversing the grating, has the greatest intensity of those measured. From this it would appear that the shape of the groove is such that most of the light for this angle of

incidence is thrown in one direction. In both spectra there is a marked diminution of intensity in passing from the shorter to the longer wave-lengths. In the spectra of the second order, the intensities are more nearly equal. The variation of intensity is, however, in the opposite direction from that in the first spectra. In both cases the general character of the curves for the two spectra of the same order is the same.

The grating from which these curves were obtained has a change in its ruling which is discernible with the eye. It was thought that there might be a connection between this defect and the peculiar character of the spectra of the first order. A second experiment was therefore performed in which the spectra from the two gratings were compared by photography. The bright-line spectrum of the carbons of an arc-light was photographed when obtained by each entire grating, also when obtained by using parts of each grating.

The only peculiarity found in the spectra obtained from the standard grating was a slight shifting of the spectrum in several cases. From the grating with the irregular ruling, the spectrum of the first order to the left was double, the two spectra being separated 0.01 inch. That of the second order was distinct and single. Both spectra to the right were double. The lines of the two spectra in the spectrum of the first order were so close as to appear like a broadening of the lines of one spectrum; in the second spectrum the two were distinct. In the case of each double spectrum, one of the spectra corresponded to the single spectrum obtained by using the irregular part of the grating alone.

From this fact, and the appearance of the grating, the double spectrum was thought to be due to a change in the number of lines ruled to the inch. The position of the spectrum indicated an increase of dispersion; the number of lines is therefore greater than the marked number, 14438. It was calculated to be 14446.

The results found in these experiments bear in the same directions with those mentioned in articles referred to at the beginning of this paper. There is nothing from which a definite conclusion may be drawn, and they therefore only serve as further evidence of a few facts with regard to gratings in general, and as a statement of some of the peculiarities of the gratings compared.

PHYSICAL LABORATORY OF CORNELL UNIVERSITY.

# A NEW APPARATUS FOR THE STUDY OF COLOR PHENOMENA.

BY ERNEST R. VON NARDROFF.

THIS apparatus is virtually an attachment that converts an ordinary projection lantern into a triple lantern in which the three beams are independent as to intensity and direction.

The beam from the lantern is first rendered "parallel," either by pushing forward the illuminant, or, better, by removing the forward lens of the condenser. In the latter case, if a physical lantern be employed having a triple condenser, no adjustment of illuminant is necessary, but with a double condenser such as is found in ordinary picture lanterns, besides the removal of the forward lens, the illuminant must be drawn back a short distance. Next, the regular focusing lens of the lantern is to be removed, and in the path of the parallel beam is to be placed the apparatus, preferably as near to the condenser as possible.

The apparatus (Figs. *A* and *B*) consists of a mahogany base supporting two uprights, to which are attached lenses, slide-holders, and diaphragms. The lenses, *a*, are auxiliary condensers, which produce images of the illuminant in the plane of the adjustable diaphragms at *d*. It is the property of such an image that each part of it receives light equally from all parts of the lens producing it, and hence the circles of light on the screen, which are images of the apertures, *p*, formed by the focusing lenses, *f*, will be uniformly dulled by partially closing the diaphragms, *d*. The focusing lenses, *f*, are mounted in sliders. By shifting these, the circles on the screen are shifted. The experimenter may thus obtain any desirable amount of overlap or separation. The range of this shifting was doubled by having the centers of the apertures, *p*, somewhat nearer together than the optic centers of the condensing lenses, *a*. These lenses, therefore, were chosen of a diameter considerably greater than the diameter of the apertures, *p*. The accurate focusing of the apertures, *p*, is accomplished by sliding in or out the broad telescopic tube, *t*, in which they are mounted. Slide-holders are placed at *k* for the reception of colored glasses, collodion or gelatin films, or glass cells containing colored liquids. Of the many colored liquids at one's disposal, I have found solutions of the sulphate, the nitrate, the ammonio-sulphate of copper, and the permanganate of potash particularly useful.

The description of a few experiments will make clear the general method of working.

Inserting in the slide-holders red, green, and blue media, and adjusting the front sliders for a perfect overlap on the screen, there is obtained a uniformly illuminated disk, probably tinted with some hue. Any attempt

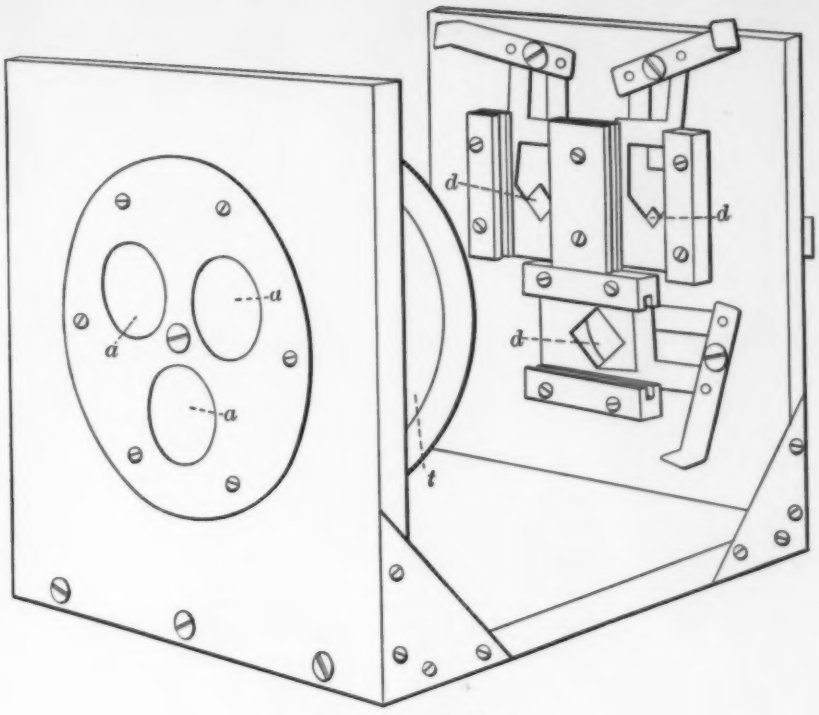



Fig. A. — Rear View.

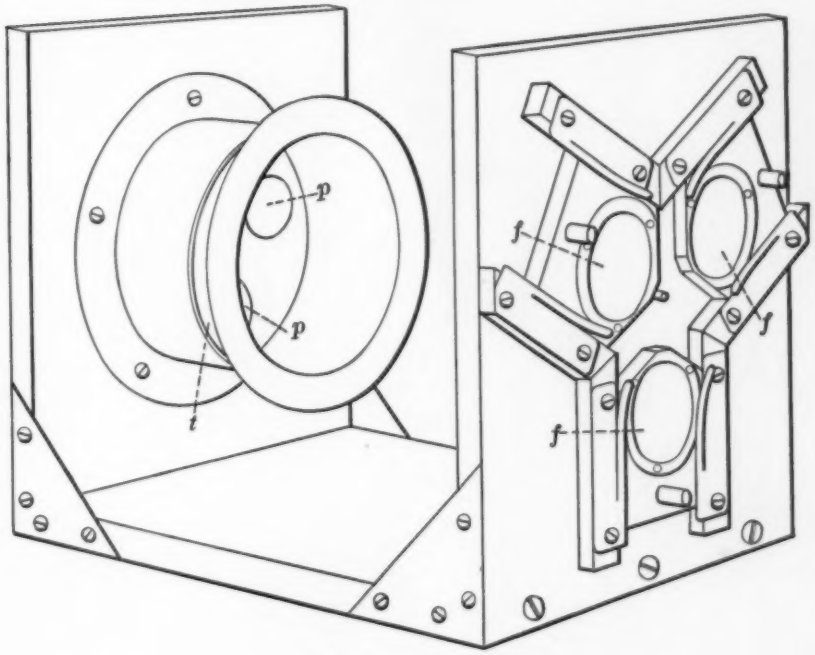



Fig. B. — Front View

to remove this residual hue by a more careful selection of color media is discouraging, because the result is so strongly affected by the illuminant, the color of which is uncertain when either the lime-light or the electric arc is employed. However, the whole difficulty is avoided by means of the adjustable diaphragms. By manipulating these, the residual hue may easily be abolished, and an absolutely pure white always obtained. This white

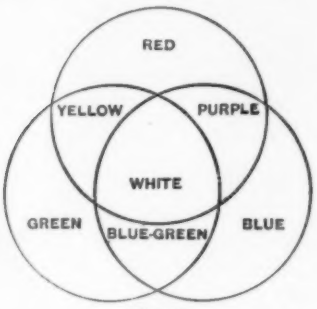



Fig. 1.

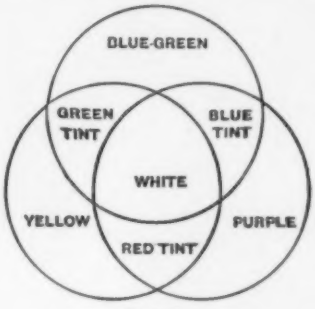



Fig. 2.

is also very intense, because its intensity is equal to the sum of the intensities of its components, instead of to their average, as with rotating colored paper disks.

If, now, the disks forming the compound white be separated in triangular fashion, the resulting figure (Fig. 1) will display the result of mixing the primaries in pairs. This mixing may be further developed by cutting off, say, the red and the blue by closing their diaphragms, leaving only the green. Then, by turning on the red gradually, and when full, by turning off the green, the overlap will pass through all gradations of hue

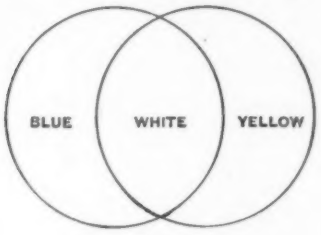



Fig. 3.

Fig. 4.

from green, through yellow, to red. The same kind of thing can, of course, be done with the other pairs of primaries.

When, instead of with red, green, and blue, we start with purple, yellow, and blue-green, we may still by proper use of the diaphragms obtain all possible hues as well as white (Fig. 2). Because the purple is a sensation that cannot be induced by light of a single wave-length, but requires a com-

plex cause, it is naturally supposed that the sensation itself is complex, and that the triad to which it belongs does not represent the primary color sensations. Further, the tints obtained by compounding these false primaries in pairs seem less pure than with red, green, and blue.

The subject of complementary hues may be illustrated by using carefully chosen pairs of color media, as in Fig. 3, or else by simply referring to the experiments of Figs. 1 and 2. There it is evident that each initial hue is complementary to the opposite compound hue.

The production of tints requires no explanation. A simple reference to Fig. 4 will suffice.

Sombre hues, such as brown, yellow-ochre, and olive-green, require a more particular treatment. On the screen, *alone*, dull red still appears red, — not a suggestion of brown, — just as dull white alone never appears gray. Sombre effects require the assistance of contrast with some standard intensity. With color disks this is present in the general illumination of the room, but with screen apparatus it must be especially supplied. The front sliders being arranged for perfect overlap, two of the slide-holders are left clear for white light, and the third is provided with some color, as red for example. A glass disk, Fig. 5, having attached to it a brass ring, *r*, and a brass disk, *d*, is adjusted in the telescope tube, and in contact with the apertures, *p*, the ring, *r*, being made to come in front of the aperture corresponding to the red glass. The diaphragm corresponding to the disk, *d*, is opened, giving on the screen a white circle having a black center. If.

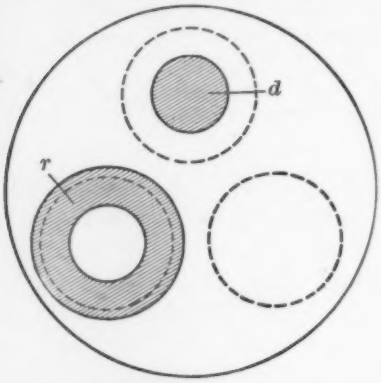


Fig. 5.

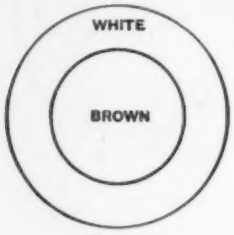


Fig. 6.

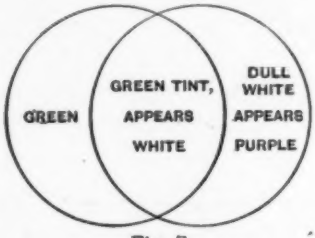


Fig. 7.

now, the red diaphragm be opened a little, a small quantity of red light will fall over the black circle, which, standing in contrast to the surrounding intense white, will appear a decided brown (Fig. 6). The effect may be

varied by turning on a little white by opening the third diaphragm; and then by using a variety of hues instead of the red, a set of tinted grays may be obtained.

Contrast effects are strikingly presented when some saturated color, as green for example, is projected and then a white disk previously arranged to partially overlap is turned on. The overlap, which is really a tint, appears nearly white, while the remaining white appears strongly colored of the complementary hue. (See Fig. 7.) If the order of projection be reversed, — the white first and then the color, — the sudden change in the appearance of the white is very impressive.

This apparatus, essentially as described, has been in use in my classes for several years, but the details have recently been much improved by Mr. F. W. Huntington, of Montclair, N. J.

## On a New Form of Water Battery.

By Louis W. Austin and Charles B. Thwing.

THE ordinary old form of water battery, consisting of zinc-copper couples dipping in short test tubes set in paraffine, while perfectly satisfactory in its working, is extremely inconvenient to fill as soon as a large number of cells are used, since each cell must be filled separately and with great care lest the insulating medium should be wetted. Some years ago Professor Rowland[1] proposed a battery, very convenient for many purposes, which consisted of a series of zinc-copper pairs cemented to the lower side of a glass plate, each pair being so near to the next that when the tips of the metal strips have been dipped in water a drop is held between each strip and the adjacent one of the opposite metal in the next pair by capillary action. This drop will evaporate in about half an hour, when of course the battery must be dipped again. If for any reason it is desired to keep up the potential undisturbed for a longer time than this, some other battery must be used.

The battery about to be described is one designed by the authors for use in some electrometer work on which they were engaged. It has proved so satisfactory and convenient in its working that we have decided to describe it for the benefit of other physicists. It is constructed as follows: The required number of zincs and coppers are cut and bent by means of a form made by driving small nails into a block of wood in the shape shown in Fig. 1. The zinc strips differ from the copper ones only in having the short bent portion at the top (*t*, Fig 1) omitted. Cuts 4 mm.

[1] Phil. Mag., March, 1887, p. 303.

deep and 28 mm. apart are then sawed in strips of dry pine wood 34 cm. long, 21 mm. wide, and about 7 mm. thick. The zinc and copper pairs are then soldered together and slipped into the cuts, after which ten strips are mounted together, with the addition of a blank strip to hold the last line of metal pairs in place in the grooved end pieces, and fastened firmly with nails. To secure perfect insulation, the wooden portions are next dipped for a few moments in a pan containing shellac varnish. The battery is completed by springing a 1-drachm homeopathic vial over each

Fig. 1.

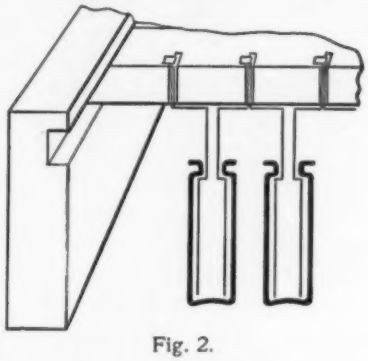


Fig. 2.

pair, the metal strips being so placed that they hold the bottles in position without any other support. The battery is filled by setting it over a pan (30 cm. by 30 cm. and 9 cm. deep) filled with water. The general appearance of one of the frames is shown in Fig. 2. In our battery ten such frames of 100 cells each are placed four deep in a portable rack of wood. A battery of this sort, while it can be filled almost as easily as Rowland's, can be used without refilling for several weeks.

THE PHYSICAL LABORATORY OF THE UNIVERSITY OF WISCONSIN,
AUGUST, 1895.

## NEW BOOKS.

*A Text-Book of the Principles of Physics.* By ALFRED DANIELL. Third edition, revised and enlarged. 8vo, pp. xxiii + 782. Macmillan & Co., 1894.

Daniell's Text-Book of Physics is adapted to the wants of students who seek a sound and comprehensive knowledge of general physics rather than the acquisition of full and accurate details of any branch of it. Numerous excellent manuals on isolated branches have issued from the press of Great Britain during the last quarter of a century, and these, to some extent, have supplanted the general text-book. But the study of general physics, in distinction from special branches, has obvious advantages, and the text-book has held its place in general education. Nevertheless the literature of physics has been no less remarkable for its poverty of English text-books than for its wealth of special treatises. The works of Arnott and Bird in England, and especially of Olmsted and Silliman in America, which fairly represented physics in the middle decades of this century, had no really worthy successors down to the beginning of the last decade. English translation took the place of English authorship. Ganot and Deschanel, in the admirable English dresses given them respectively by Atkinson and Everett, held almost universal sway until 1884, when Daniell's Physics first appeared.

It was Balfour Stewart, I think, who first broke away from the traditional method of treating physics in disconnected fragments, and courageously presented the science of matter and energy. But Balfour Stewart's work was a small volume adapted to younger students. Daniell, viewing physics in the light of the same great truth, but from a standpoint fourteen years higher than that of Stewart, redrew the science in bolder outlines, on a larger scale, more elaborate and adapted to maturer readers. A third edition of this standard text-book, carefully revised and considerably enlarged, is now before us. A glance along its pages reveals the fact that the spirit and method of the book have not been changed. But the work of revision may be seen everywhere. Sometimes it is detected in the change of a word; sometimes in the remodelling of a sentence; and sometimes in the recast of a paragraph. In some cases it is found in the extension of a discussion to a more general conclusion; in others, in the incorporation

of subject matter which is entirely new. The motive of it all is easily discovered. Greater accuracy and precision have been secured, important gaps have been filled, and the later results of research have been embodied. The limits of this review forbid more than a brief record, with scant illustrations of a few selected features of this revision.

A very welcome modification of the notation has been made. To each physical quantity a symbol is assigned which, as far as possible, it retains throughout the book. Quantities in general are represented by capital letters, while quantities per unit area are designated by the corresponding small letters. Mr. Heaviside's suggestion that blackfaced type be used for directed quantities has been adopted, and other devices in type furnish other distinctive characters. A two-page "index of symbols," in which every character in this system is explained, is thoughtfully supplied. Why may not this effort be extended to the literature of physics in general? The adoption of a uniform and carefully adjusted system of notation is next in importance to the adoption of a uniform system of units.

We notice next the incorporation of recently suggested terms, such for example as inductance, conductance, and impedance; permittance and permittivity for electrostatic and specific electrostatic capacity. Magnetomotive force, magnetic flux, and reluctance appear with their units, and their relation, analogous to Ohm's law, is pointed out. The work of the international congress, Chicago, is referred to in the appendix as recommendations only, but the henry is placed among the practical units without reserve. Among the properties of matter we find shearability as the reciprocal of rigidity, cubical compressibility as the reciprocal of elasticity of volume, and in another connection we find dilatancy to designate the change in volume which accompanies change in shape of granular masses.

Another motive appears throughout the work which, I think, cannot be too highly commended. I refer to the author's anxiety to impart clear-cut conceptions of physical quantities and to protect the student from the pernicious influence of ambiguous terms. Think of the difficulties fostered by the long-time vague use of the word *force*. The author tries to avoid them by rejecting absolutely the notion of force as a physical entity, and using the word as a convenient term to designate a measurable quantity — the mutual action of bodies. Think of the inaccuracies involved in the ordinary use of the word *weight*. The author would forestall them by defining weight as a measurable action, assigning to it a symbol $G$, representing its value in a formula $G = ma$, and recording its value in dynes. Think of the confusion incidental to the use of one term in many senses — a most common and distracting feature of physical nomenclature. The author would preclude it, if possible, by setting the several uses of each ambiguous term precisely before the student. "We shall, except where

the context makes it plain, avoid the use of the unqualified word *stress*, and endeavor to make it clear whether in any particular instance we refer (1) to a condition of stress, (2) to a stress of so many dynes, or (3) to a stress of so many dynes per square centimeter" (p. 24). The several meanings of an overloaded term are sometimes compiled, with a reference number given to each. In the list for pressure no less than five are formulated (p. 25).

There is a gratifying extension of the text to cover the later researches. This feature of the revision is especially marked in the chapter on electricity. Thus we find new paragraphs on the ether as the universal medium involved in the phenomena of electricity, magnetism, electro-magnetism, light, radiant heat and actinic radiations. New pages are devoted to electric waves, Maxwell's theory, and the inferential properties of the ether, oscillating currents, dynamo machines, and the transmission of energy to a distance. This last-named subject is too briefly treated, and Tesla's motives and successes receive scant recognition.

To those who have yet to make acquaintance with this treatise a brief *résumé* of its contents may be useful. An introduction supplies the axiomatic truths and fundamental laws on which physical investigation is based. The work then opens with a discussion of measurement as the foundation of all accurate knowledge of phenomena. One short chapter is devoted to the fundamental units of time, space, and mass; another to the derived ideas of motion, velocity, acceleration, momentum, and force as measurable quantities; a third describes in general terms some practical methods adopted in the measurement of those quantities; while a fourth discusses work and energy, giving definitions of their units and the law of conservation.

A second group of four chapters follows, based on the doctrine of energy, and devoted to the principles of kinematics, kinetics, potential, and gravitation. Harmonic motion and the propagation of waves, potential and the conception of space as a field of force, are here discussed with sufficient fullness and great care. The older problems also, — acceleration and rotation, impact and friction, moments and mechanical powers, gravitation and the pendulum, — are examined in the light of the all-pervading principle of energy.

These two groups of chapters, I. to VIII. inclusive, may be regarded as a preparatory course. While they keep the problems of the material world constantly in view, they withhold the student from an immediate attempt to grapple them. Filled with fundamental principles, definitions, and physical conceptions, they are the armory and drill-ground where the student may get an adequate equipment and training. In Chapter IX., for the first time, the study of physics as a science of phenomena comes to the front.

A third group of four chapters here begins, which is devoted to the study of matter. They comprise, in general, a discussion of its properties, states, and constitution; and then, in particular, the special features of solids, liquids, and gases. These chapters fairly bristle with modern views. Ether takes its place among the states of matter. Molecular structure, viscosity, the critical state, and the kinetic theory are prominent. The conception of matter as substantially one thing, and of its different forms and states as incidental variations determined by the energy which each body is, for the time being, the reservoir, cannot escape the thoughtful reader.

Following these is a fourth group of four chapters, discussing the phenomena of energy under the titles of heat, sound, ether waves, and electricity and magnetism. The discussion of heat is brief. One is somewhat surprised to find so much of so large a subject in so small a space. But as heat is a form of energy, the principles relating to heat may, to a great extent, be extracted from the general principle. This is the secret of the author's successful brevity. The propositions relating to heat are set in the doctrine of energy, like crystals of metal in their native vein-stone. The student will sometimes find his strength and skill severely taxed to think them out. The chapter is not an easy one. The next, on sound, is fairly well written, discloses the essential features of the subject, and is quite full on pitch and temperament. It permits close thinking, but does not seem to compel it. Not so with the chapter on ether waves. One must in the outset learn to think of ether as he thinks of air, — a medium whose reality is to be admitted as an inference from the phenomena to which it gives rise. The reader must firmly grasp the difficult conception of ether motions and ether stresses, and as he has already learned to look upon bodies of matter as reservoirs of energy, so must he now behold ether as the vehicle for its transfer.

Beginning with the nature of radiations, the path leads on through color, Prevost's law, Stoke's law to spectrum analyses. Starting again with molecular vibrations, we follow the propagation of waves through ether, taking, on our way, the phenomena of plane polarization, reflection, refraction, interference, double refraction, to elliptical and rotary polarization, where we halt to discuss optical instruments and visual perceptions. Finally, in the last and longest chapter, the principles of electricity and magnetism are discussed with considerable detail, the omnipresent ether being invoked to unitize the whole. The time will come, no doubt, when this can be done with more complete success than seems to be possible at the present time.

The specialist need not consult Daniell's Physics for technical details. The mathematician need not go to it expecting to find a mathematical gymnasium. The historian will miss the descriptions of classical experi-

ments and the narrations of personal achievements. But the student of science will find it to be a cabinet of well-selected facts, mathematical reasonings, and experimental results, skillfully arranged to exhibit the system of principles that underlie physical phenomena.

LEROY C. COOLEY.

*Solution and Electrolysis.* By WILLIAM CECIL DAMPIER WHETHAM, M.A. pp. viii+296. 19 illustrations. Cambridge, The University Press; New York, Macmillan & Co.

During the last few years the scientific advances made in physical chemistry have been marvelously rapid, and especially has this been the case in those lines which relate to solutions and electrolysis. Questions present themselves to the investigator from all sides of the subject, and their solutions are often within the reach of limited apparatus and limited time on the part of the investigator. As a result, the periodical literature is rich in memoirs on the subject. It is therefore not surprising that there are many general scientific readers who are incapable of following some of the later memoirs. To such persons the present volume will be welcome. It will also be of great value to the specialist in this line, because of its suggestiveness, and especially because of the tables at the end.

The book, as its title indicates, has two distinct parts. The first part covers six chapters. In them the kinetic theory of solutions is presented in very much the same manner as in Muir's translation of *Ostwald's Solutions*. The numerical results of experiment are omitted except occasionally, where their presence makes the presentation of the subject clearer. The five remaining chapters are devoted to electrolysis. In the first of these the early work of Davy, Faraday, and Grotthus is described, and the theory of primary and secondary batteries is presented. In connection with the latter, a paragraph on polarization appears, which makes no reference to the work done during the last fifteen years. Chapter VIII. is devoted to the ions — their nature, their migration, and their velocities of migration. Chapter IX. is concerned with the conductivity of electrolytes. At this place the dissociation theory of Arrhenius is introduced. Throughout the second paragraph of the chapter *potential differences* are wrongly called *electromotive forces*. Bouty's method of determining the resistances of electrolytes is described and illustrated. The prominence given to it constitutes a recommendation. Yet Bouty was led into false conclusions from its employment; and, as Kohlrausch stated (*Annalen der Physik und Chemie*, Band XXVI., p. 219), it is surprising that his results were as good as they were, considering the liability to temperature errors. The *convenient*

form of electrolytic resistance vessel represented in Fig. 18 will hardly be considered so by American workers. The following chapter is devoted to the consideration of the connections existing between electrical conductivity, chemical activity, and osmotic pressure. The last chapter is devoted to the theories of electrolysis.

A reprint from the report to the British Association for the Advancement of Science, of a table of electro-chemical properties of aqueous solutions, compiled by the Rev. T. C. Fitzpatrick, occupies the last sixty-nine pages of the book. This will prove of great value to investigators. All ordinary electrolytes are considered in it, and a mere inspection serves to determine any data concerning equivalent composition, specific gravity, electrical conductivity, migration ratios, and fluidity constants. The specific molecular electrical conductivities are given in terms of the true ohm as well as of the mercury unit.

SAMUEL SHELDON.

*Polyphase Electric Currents and Alternate-Current Motors.* By SYLVANUS P. THOMPSON. 8vo, pp. vi, 261. New York, Spon & Chamberlain, 1895.

The author assumes that the reader is familiar with the general principles of alternate currents, and begins the book with a chapter on polyphase generators. In this treatment engineering requirements, details, and data are largely omitted, and the student's attention is directed to the physical principles and characteristics of this class of machinery. Brief references with illustrations are made to the productions of various manufacturing concerns.

The next chapter deals with the combination of polyphase currents, and a similar treatment in the latter part of the chapter is applied to combinations of magnetic fields. The first part of this chapter is useful and to the point. I regard the latter part as unfortunate, since at this time it is no longer necessary to use the rotating field hypothesis when dealing with the induction motor. The author's evident purpose is to prepare the reader to accept, in lieu of the polyphase alternating field, a simple rotating field of one or more pairs of poles.

As further evidence of the practical identity of polyphase alternating fields and simple rotating fields, the reader witnesses in Chapter III. experiments with both forms of field. Much attention is paid to their similarity, and none to their differences, — differences of importance in much engineering design and construction.

The chapter devoted to the early development of the polyphase motor is excellent. It recites the early experiments that led men to investigate

the properties of polyphase alternating fields similar to those of simple rotating fields. This chapter, however, unfortunately leaves the reader with the impression that symmetrical polyphase alternating fields and simple rotating fields are practically identical, and that the modern induction motor results from a recognition of these facts.

Chapter V. is probably a good description of European induction motor practice. Excepting a reference to Tesla's early experiments, nothing is said about American practice. Yet this country has produced at least three of the best forms, based rather on improvements that result from a transformer or rational study of the induction motor, than on the teachings of the rotating field hypothesis.

Chapters VI. and VII. are largely of historical value, as they present the hypothetical considerations which led to the ultimate development of the modern induction motor, and are not the working theories of the engineers who are producing the practice of the present day. The theories of this chapter would never lead to the production of an efficient monocyclic motor, nor show the important part that is played by the mechanical motion of the secondary conductors in the production of the back electromotive force.

The reference to monophase motors is quite complete and well done. The last chapters, after a brief and sufficient discussion of polyphase transformers, illustrate the application of the rotating field hypothesis for purposes of practical design, and close with some examples of European polyphase practice, including details of modern Oerlikon polyphase motors.

A highly valuable feature of this work is the complete bibliography given in Appendix I.

This book has in it much of value, as the high standing of the author warrants; nevertheless, we do not see why so much of importance belonging to American practice is absent. Doubtless distance, and the rapid rate at which the practice is developing, may in part account for this.

HARRIS J. RYAN.

*Industrial Photometry with Special Application of Electric Lighting.* Translated from the French of Palaz, by GEORGE W. PATTERSON, Jr., and MERIB ROWLEY PATTERSON. $4.00. pp. 322 + vii. New York, Van Nostrand, 1894.

This is a translation of the well-known work of Palaz, a notice of which has already appeared in the pages of the *Review*.[1]

It is, in the main, an excellent translation. The original has been closely

[1] Physical Review, Vol. I. p. 238.

followed article by article, and a work, which in the French was remarkable for precision and clearness of statement, has been placed at the disposal of English readers in such a form that these valuable characteristics are not lost. Occasionally, however, the author lapses from complete lucidity, and the translators go with him. On pages 8 and 9, for example, we find a table in which the approximate limits of the ultra-violet, and visible regions, and of certain regions in the infra-red of the spectrum are gathered under the heading "Character of the vibratory movement."

More frequently the translators record their disagreement with the author by means of brief notes in an appendix. This, on the whole, is a plan to be commended, since the form and arrangement of the original is nowise disturbed. Where, however, it is a question of an obvious correction, as in the case in which the absorption by a mirror is given at 1.8 per cent instead of 18 per cent, a better place to note the error would have been in the text or in a footnote upon the same page.

It should be noted that Professor Ayrton's paper on the arc light, to which reference is made in section D of the appendix, is unfortunately not to be found in the *Proceedings of the Chicago Congress*, nor elsewhere. The manuscript was accidentally destroyed before it reached the hands of the editing committee.[1]

The most important portion of the appendix is the set of regulations for testing the Hefner lamp. These have been translated from *Schilling's Journal*. A few addenda from the personal experiences of the translators have been made in the body of the text, as, for example, where the method of studying glow-lamps pursued in the University of Michigan is described. These additions are not such, however, as to modify the character of the book.

Owing to the conservative treatment, the strong points of the original treatise, namely, the description of photometers and of photometric standards, with the data concerning the latter, remain the most important points of the translated work. Those portions of the subject which were weak or defective in the original, as, for example, questions of spectrum photometry and the study of differences of quality of light, have not been reinforced. It is not, however, the normal function of the translator to remodel the work which comes under his hands, and doubtless it is to be preferred that the original should be closely followed even to the point of perpetuating its weaker elements. New matter, excepting such as may be casually introduced in the form of an appendix, had better form the material for a distinct treatise.

E. L. NICHOLS.

[1] An abstract of the most important points will be found in a paper by Mrs. Ayrton. Electrician, Vol. 34, p. 335.

*Die Oberflächen- oder Schillerfarben.* Von B. WALTER. 8vo, pp. vi + 122. Braunschweig, Vieweg & Sohn, 1895.

This monograph upon the nature of surface color is intended primarily for zoölogists, mineralogists, and chemists, one of the purposes of the author being to point out that many of the colors which are usually ascribed to structure of the surface layer, and which are classified either as colors of thin plates, of grating-diffraction, or of prismatic dispersion, are really true surface colors.

To this end, the laws of the formation of surface color by reflection are taken up in a clear and simple manner, and it is shown that bodies, otherwise colorless, possess a *surface color* due to the fact that the intensity of each reflected wave length depends upon the refractive index of the reflecting body for that particular ray. Since the index varies with the wave length, the composition of the reflected differs from that of the incident light. This is a perfectly obvious matter, but rarely considered in the discussion of color formation. Dr. Walter computes the differences in intensity between red and violet of the reflected light, and shows that in the case of bodies producing high dispersion it is considerable. By normal reflection from carbon disulphide, for example, the violet ray gains 16 per cent over the red of the spectrum.

At the interface between certain substances which differ greatly in dispersive power, as, for example, between crown glass and oil of cassia, this color, due to reflection, becomes very marked. The violet may become three times as intense as the red in the reflected ray.

The succeeding portions of the monograph deal with the surface colors of metals and of the real "Schillerstoffe." These last are substances which absorb a single region of the visible spectrum strongly, other parts scarcely at all. Fuchsin is one of the best known of this class. The colors of these also are shown by the author to be colors of reflection; and, finally, in his concluding chapter, he shows that many of the colors of animals and minerals, which are ordinarily ascribed to interference, are really surface coloring, and ascribable to reflection. The work is a valuable contribution to the science of color.

E. L. NICHOLS.

*The Herschels and Modern Astronomy.* By AGNES M. CLERKE. $1.25. 12mo, pp. vi + 224. London, The Century Science Series, Cassell & Co.; New York, Macmillan & Co.

Miss Agnes Clerke, whose work upon the history of astronomy has rendered her an authority, is admirably equipped for writing the biography of the Herschels. A more attractive theme to the lover of biography than

the relations of this remarkable family to the development of modern astronomy, it would be difficult to find. The story of the rise of the elder Herschel from the position of an oboe player in a Hanoverian military band to that of court astronomer to King George, is one to excite the warmest sympathy and interest on the part of the reader. The sketch of Caroline Herschel is scarcely less interesting than that of her brother. The position which she has held in the minds of many is simply that of an untiring assistant in the computing room of the astronomer; Miss Clerke's portrait reveals to us a woman of great versatility and of great strength of character, a woman to whom the reader feels strongly drawn.

The interest of the book centers in the history of William and Caroline. When we come to Sir John Herschel there is a distinct falling off. The elder Herschel won scientific fame as other poor men sometimes win fortune. John Herschel inherited his position in the scientific world as men inherit money, and with it definite work in astronomy which he deemed it his duty to undertake and carry to completion. The magnificent manner in which he fulfilled the scientific obligations which he inherited from his father is well described in the pages of this brief memoir, but it is impossible to imbue such a career, however brilliant, with the romantic interest which one feels for the heroic upward struggle of the founder of the house.

E. L. NICHOLS.